A NOVEL CLASSICAL SYNTHETIC APPROACH TO CARBON NANOTUBES AND THEIR FUNCTIONALIZED DERIVATIVES

by

BERNARD WIREDU

B. S., UNIVERSITY OF GHANA, 2000

AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the requirements for the degree

DOCTOR OF PHILOSOPHY

Department of Chemistry
College of Arts and Sciences

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2008

Abstract

Carbon nanotubes are allotropes of carbon comprising of one or more grapheme sheets seamlessly joined together to form a cylinder. They are classified as single-walled carbon nanotubes (SWNTs) or multi-walled carbon nanotubes (MWNTs). They have potential applications ranging from conductive and high reinforcement material components, nano interconnection in electronic devices to drug delivery in biological systems.

Current methods of production are high temperature arc-discharge, laser ablation of graphitic materials and chemical vapor deposition. These methods give tubes that are impure and highly heterogeneous in length, diameter and chirality thus leading to mixture metallic and semiconducting tubes. Effective application of such carbon nanotubes requires cumbersome, harsh and expensive purification and sorting into like forms. Such treatments usually compromised the structural integrity of the tubes and hence their mechanical and electrical properties.

Also pristine carbon nanotubes are insoluble in most solvents. Solubility in basic organic solvents is crucial prior to their application, which requires some level of chemical manipulation or functionalization on the tubes. Currently methods of functionalization are unpredictable and limited to few oxidation reactions.

A novel rational synthetic chemical approach to [12, 12] arm-chair carbon nano tube with pre-defined diameter and length has been explored utilizing cheap and simple organic building blocks and results achieved so far have been presented in this dissertation. Two approaches were employed to form the carbon-rich beltene (**32**) before its final conversion to the target single-walled carbon nanotube (SWNT) **1**. A survey on carbon nanotubes and their related structures including their potential applications and properties are presented in chapter 1.

In the second chapter an iron template-assisted olefin metathesis via a ferrocene intermediate served as an anchor for an effective cyclization. In chapter 3, an un-assisted olefin metathesis pathway was explored. Both approaches use a series of benzyl halide carbonylation coupling and Diels-Alder reactions to synthesize some of the key intermediates.

The protocol presented in this dissertation may be used to produce functionalized carbon nanotubes with predefined length and diameter tailored for specific applications to be produced in kilogram scale for the first time since its discovery in 1991. Such an approach is expected to address most if not all of the problems associated with the traditional methods of producing carbon nanotubes.

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Approved by;

Major Professor
Dr. Duy H. Hua

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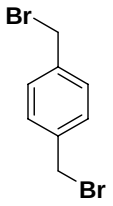
Structure – number correlation list



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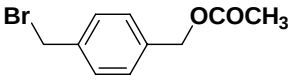

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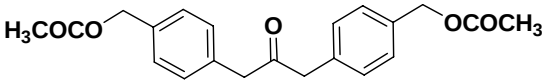

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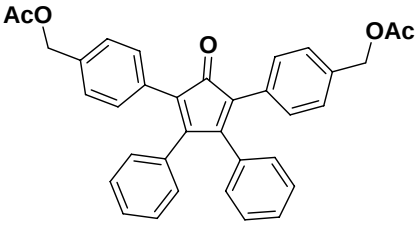

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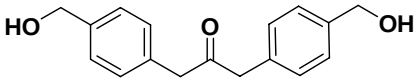

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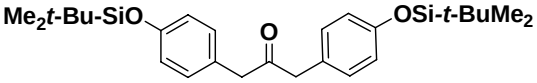

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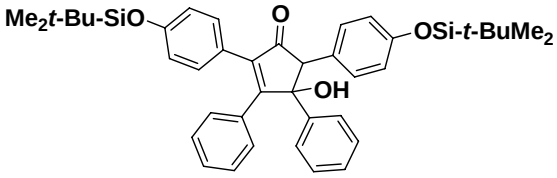

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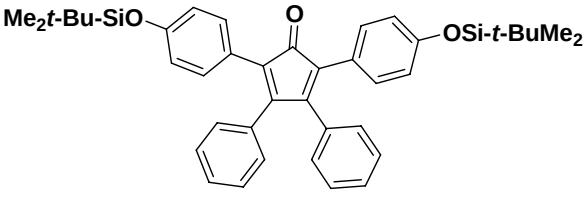

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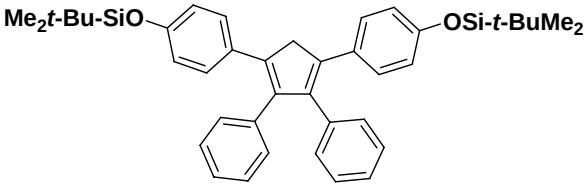

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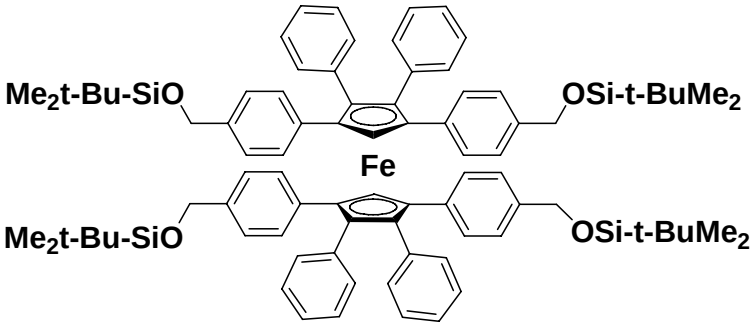
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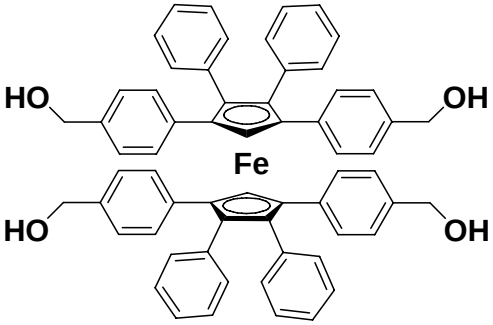
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HO
OH

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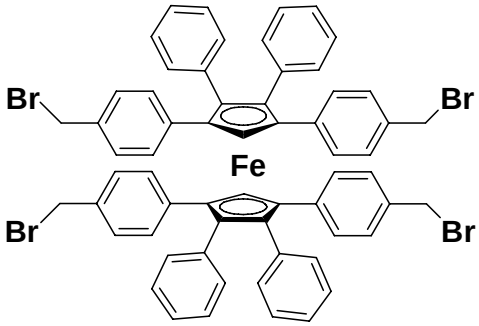
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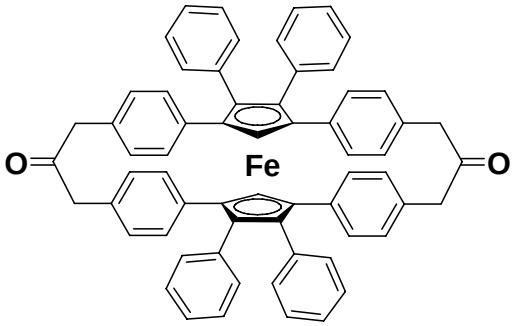
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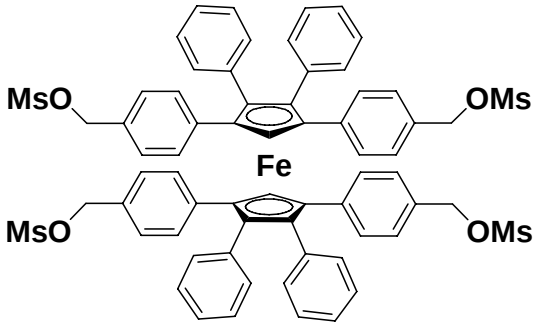
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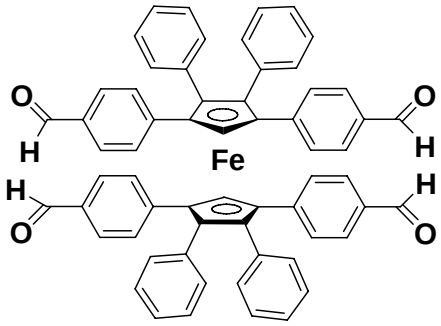
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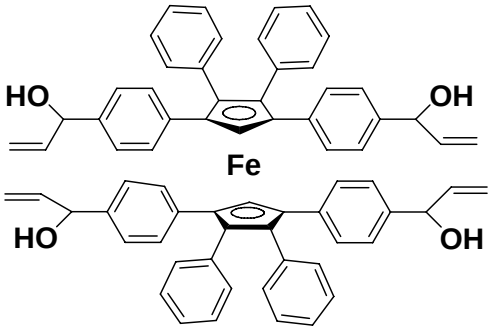
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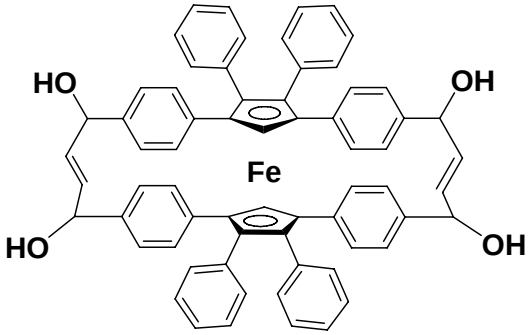
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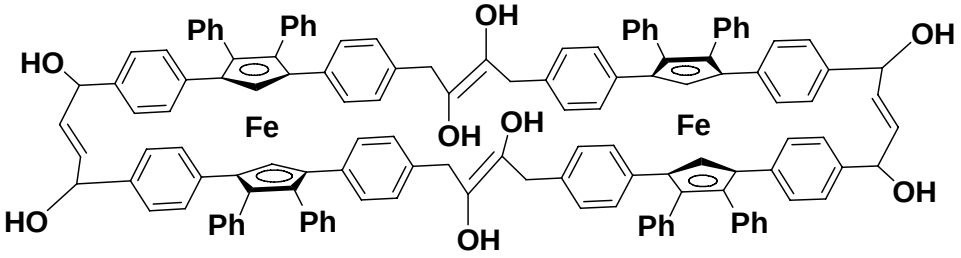
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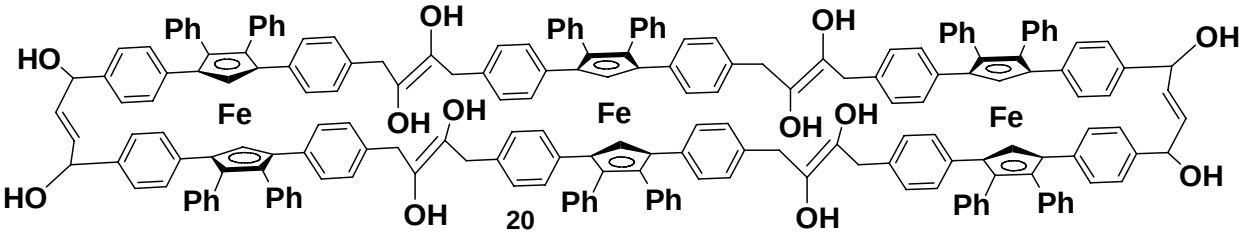
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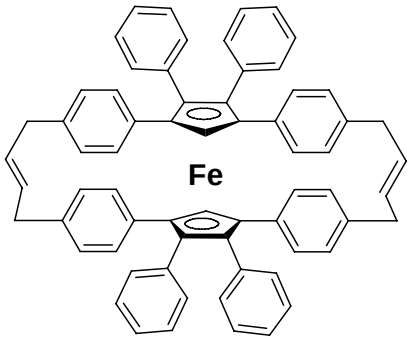

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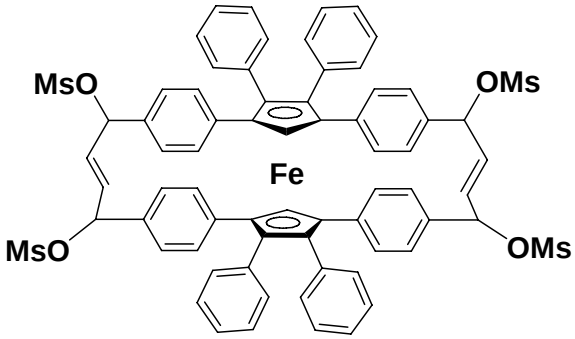

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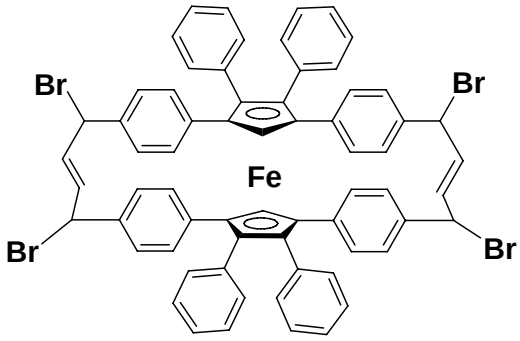

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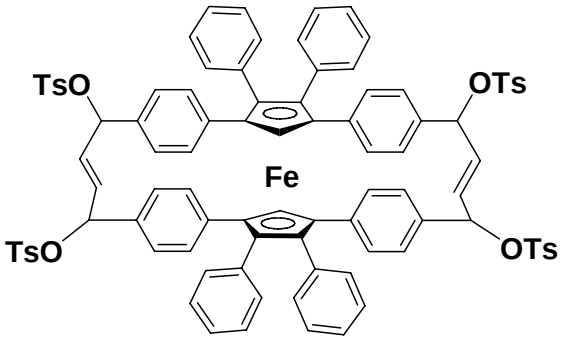

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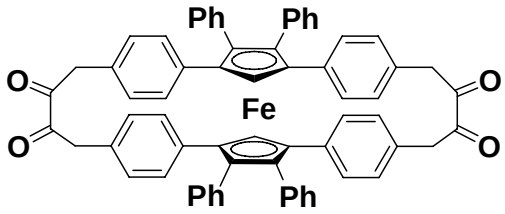

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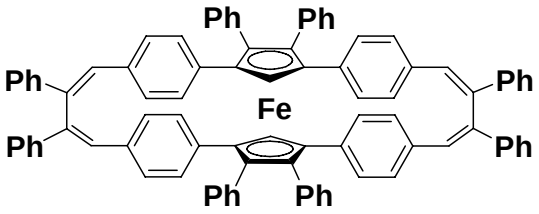

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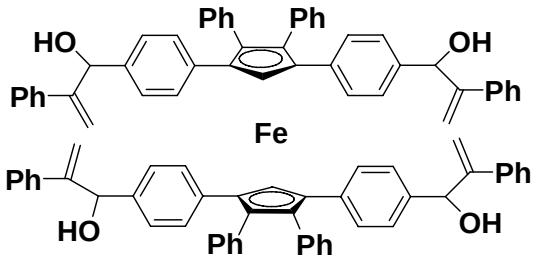

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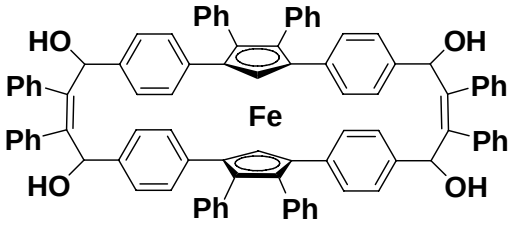

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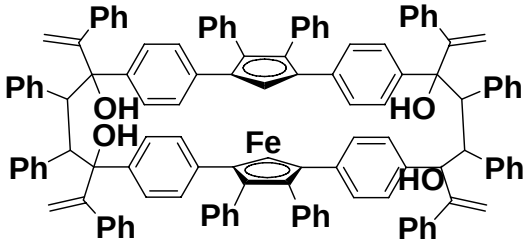

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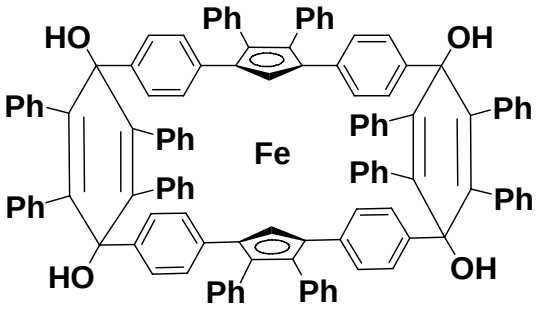

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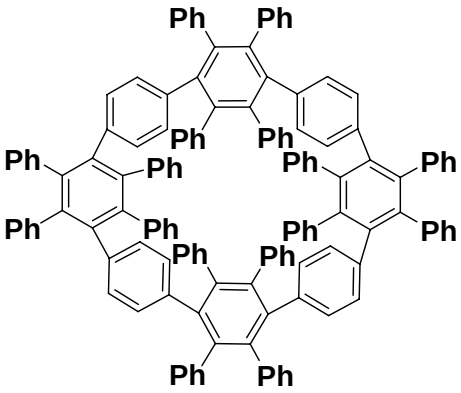

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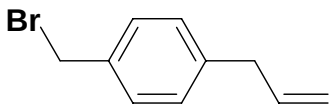

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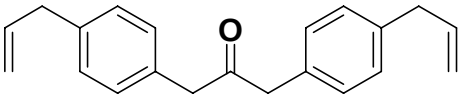

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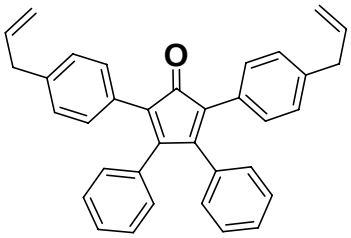

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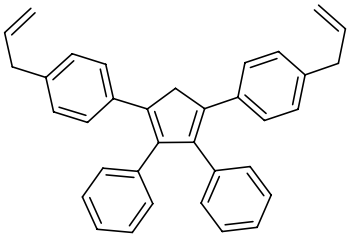

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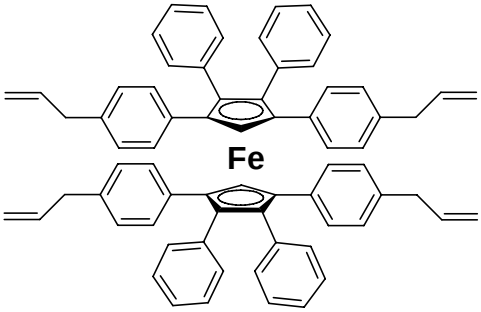

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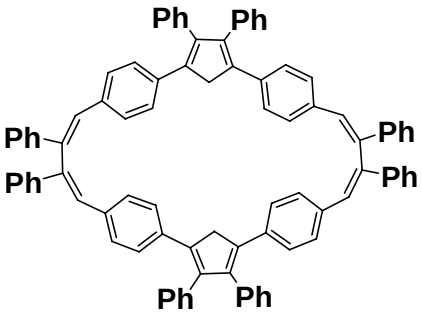

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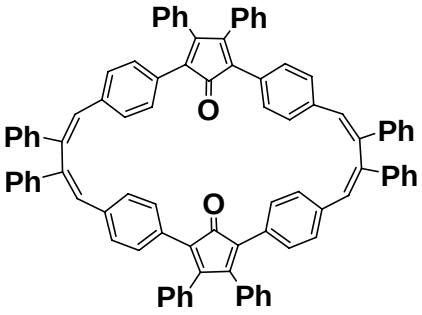

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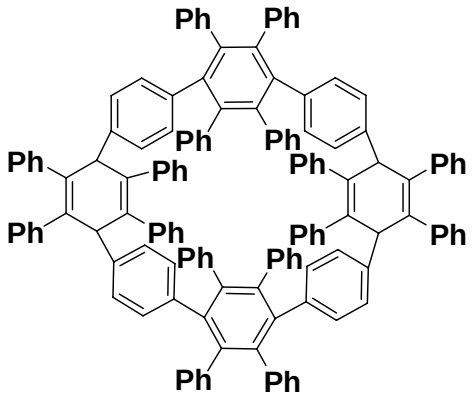

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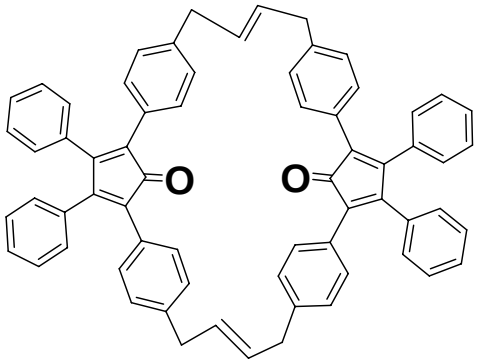

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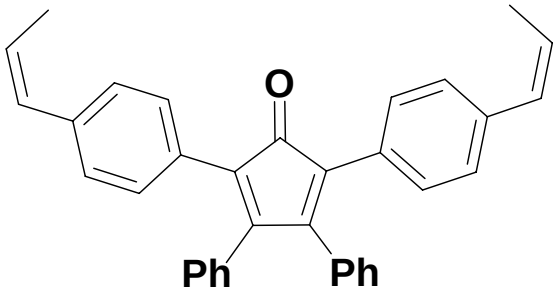

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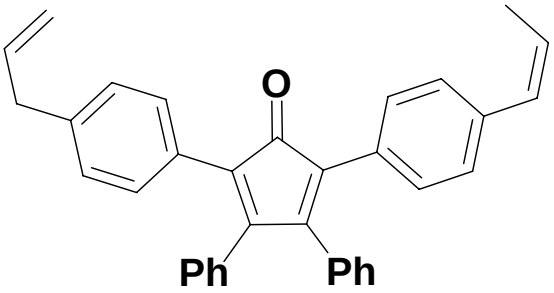

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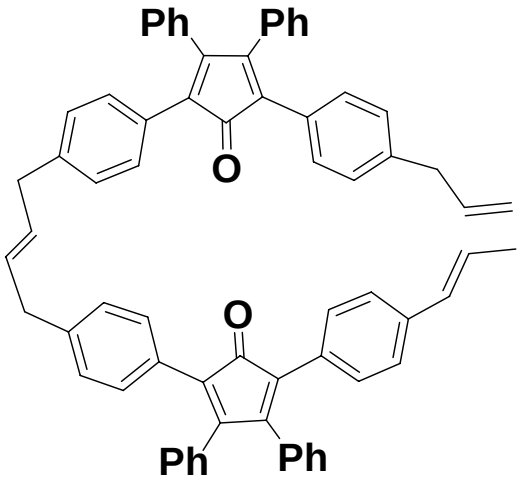

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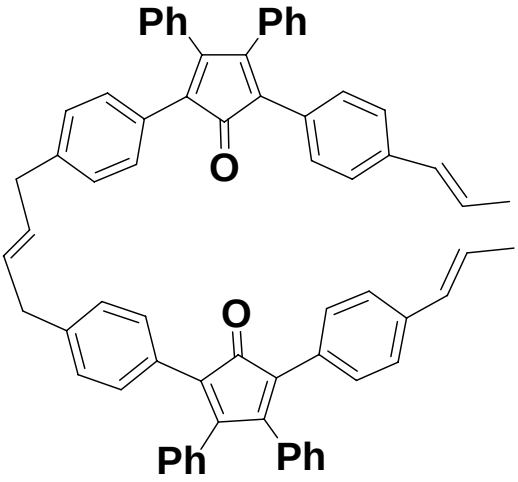

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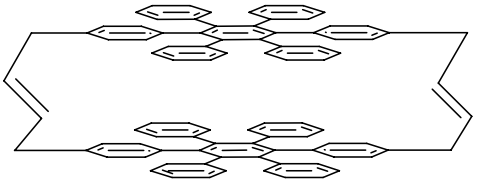

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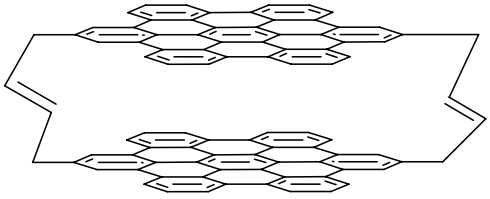

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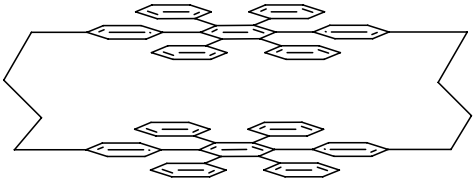

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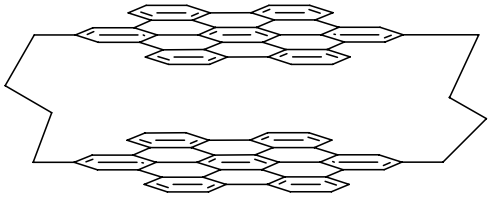

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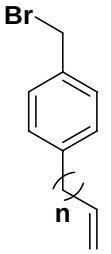

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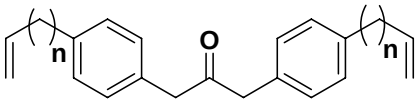

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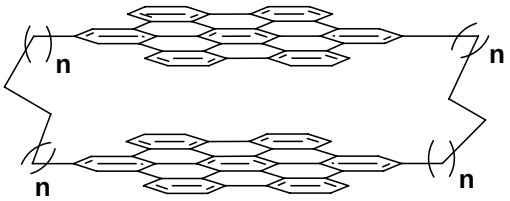

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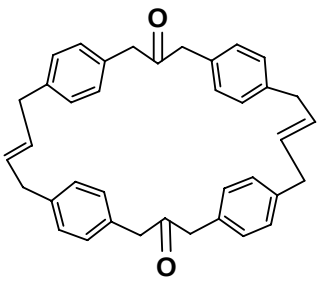
n = 2, 3, 4 etc



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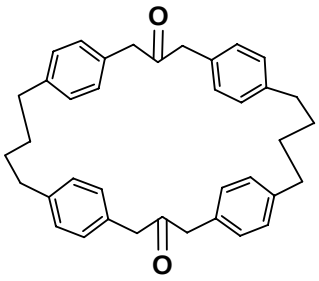

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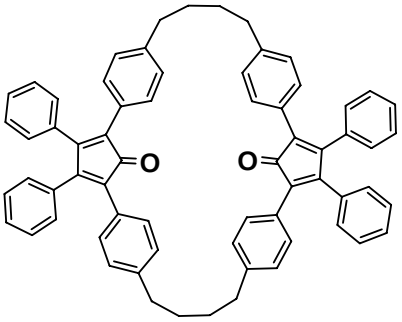

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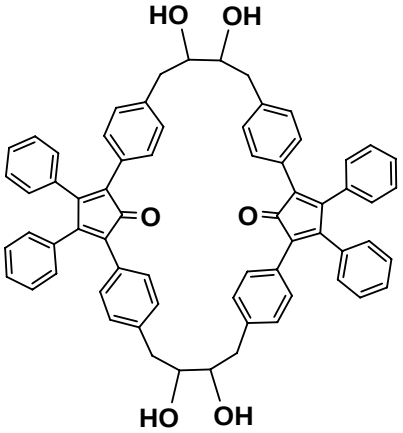

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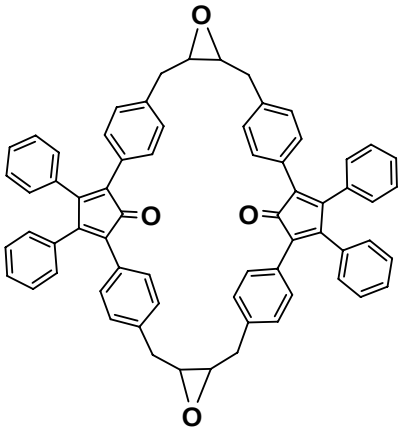

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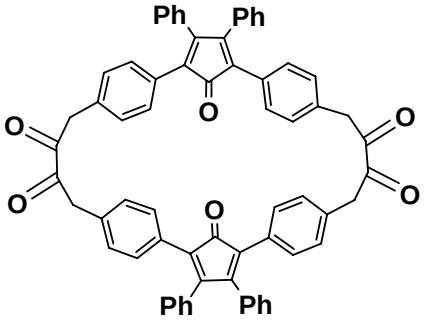

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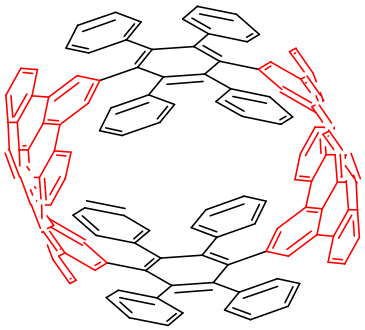

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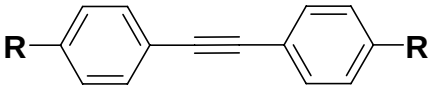
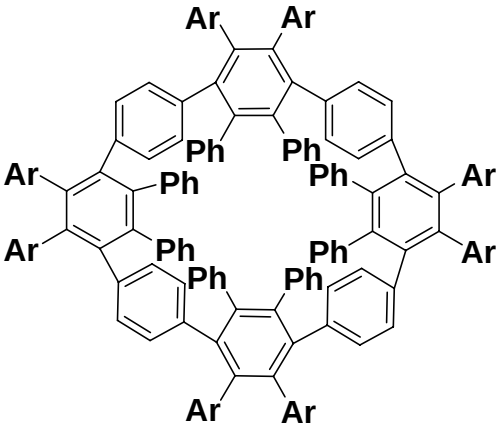


60: R = Br

61: R = OAc

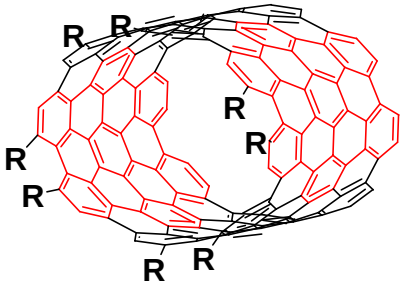
62: R = NHAc



63: Ar = 4-BrC_6H_4

64: Ar = 4-AcOC_6H_4

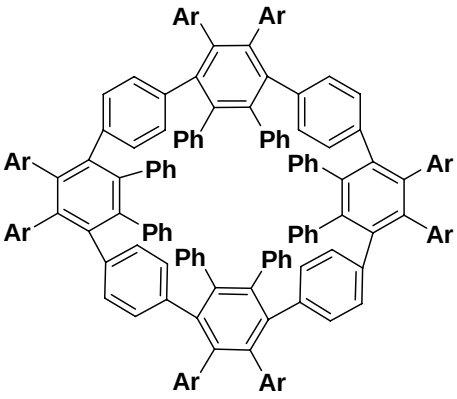
65: Ar = 4-AcNHC_6H_4



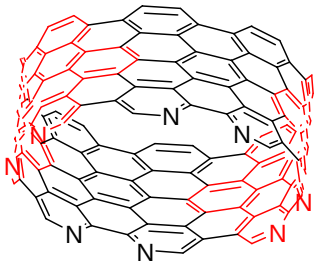
66: R = Br

67: R = OAc

68: R = NHAc



69: Ar = 3-pyridyl



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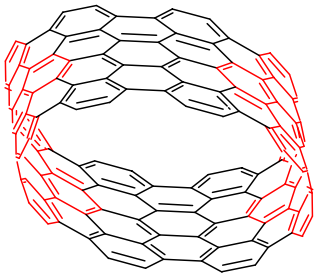

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My deepest thanks and appreciation goes to my wife for always being there for me and taking care of me. Special thanks go to my Church family in Manhattan, KS

Finally I thank God for sustaining my life in all this.

Dedication

To

Mary and Kevin Wiredu

List of abbreviations

Ac	acetyl
AcOH	acetic acid
Bn	benzyl
BuLi	butyl lithium
^{13}C-NMR	carbon nuclear magnetic resonance
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMAP	4-(*N*,*N*-dimethylamino)pyridine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
Et_2O	diethyl ether
Et_3N	triethylamine
EtOH	ethanol
^{1}H-NMR	proton nuclear magnetic resonance
HRMS	high-resolution mass spectrometry
IBX	*o*-iodoxybenzoic acid
LAH	lithium aluminum hydride
LDA	lithium diisopropylamine
m-CPBA	*meta*-chloroperbenzoic acid
Me	methyl
MeCN	acetonitrile
MeOH	methanol
MsCl	methanesulfonyl chloride
NBS	*N*-bromosuccinimide
NMO	*N*-methylmorpholine – *N* - oxide
OAc	acetate
OMs	mesylate
OTf	triflate

Ph	phenyl
PPh_3	triphenylphine
pyr	pyridine
RCM	ring closing methathesis
rt	room temperature
TBAF	tetra-n-butylammonium flouride
TBDMS	*tert*-butyldimethylsilyl
t-Bu	*tert*-butyl
THF	tetrahydrofuran
TLC	thin layer chromatography
Ts	*p*-toluenesulfonyl

CHAPTER 1 - CARBON NANOTUBES AND RELATED STRUCTURES

1.1 Introduction

There were evidence of the existence of some materials that at least bore resemblance to carbon nanotube and nano-particle before the 1991 discovery by Iijima. These have been worked on and reported by various authors as early as the 1950's.[1]

However, these early pioneers largely fail to recognize the enormous potentials of these materials in addition to difficulty and conflicting characterization by these pioneers until the work of Iijima who is largely credited with the discovery of carbon nanotubes were published in the early 1990.[2]

One of the earliest publications on carbon nanotube related materials was published as far back as in 1953 by Davis et al.[3] They employed the use of catalytic methods by reacting carbon monoxide and an oxide of iron (Fe_3O_4) at 450^{o}C to produce a thread-like carbon material, which have been claimed to be identical to carbon nanotubes. However, careful scrutiny of Davis's structures reveals significant difference between them and the carbon nanotubes as described by Iijima in 1991 in terms of structure, morphology and function.[1]

A scroll-like carbon similar and related to carbon nanotubes both in production, constituent and potential applications referred to as graphite whiskers were also discovered in the later part of the 1950's by Roger Bacon.[4, 5] However, a closer look at graphite whiskers and carbon nanotubes reveals an overwhelming difference between them.[2]

Graphite whiskers were found to have properties closer to that of perfect graphite than to carbon nanotubes and are made up of concentric tubes having the form of a scroll, strong and more flexible having an average tensile strength and modulus value of 20 GPa and 1 TPa respectively.[4]

Figure 1.1: Schematic representation of a scroll-type graphite whisker[2,4,5]

Besides the above-mentioned evidence of carbon nanotubes and materials, a lot more remain scattered in the various scientific journals before 1991 about some form of carbon related materials or shells which are now being claimed to bore some form of resemblance to carbon nanotubes.[1, 2]

1.2 CARBON NANOTUBES: WHAT ARE THEY?

Carbon nanotubes are single-dimensional, seamless array of cylindrical sheets of graphene. A typical diameter ranges from 1-30 nanometers and lengths of up to several microns. Consequently, they exhibit very large aspect ratios (length/diameter) generally greater than 100.[18] In general shorter carbon nanotubes are more preferable since they lend themselves easily for further chemical manipulation for various applications. Essentially, they are regarded as allotropes of carbon. They were found to grow on the surface of the graphite cathode during the arc-discharge process production of fullerenes mixed with amorphous carbon. Carbon nanotubes

can be metallic or semi-conducting. This property depends on the arrangement of the hexagon rings along the tube surface in the direction of the tube axis.[18]

There have been records of many classes of either organic or inorganic tube-like materials which are projected to have interesting electronic and mechanical properties.[19,20] Among these, the class of carbon nanotubes and related carbon nano particles has shown enormous promise for myriad of applications in material and medicinal chemistry.[19] Other important potential applications for carbon nanotubes in nanotechnology include their use as fillers in polymer matrixes, molecular tanks for hydrogen storage and biosensors.[6,21] However, their poor or lack of solubility in most organic solvents and aqueous media has become the major drawback to the rapid acceleration in realizing many of its potential applications in industry as fast as expected judging from the level of enthusiasm and enormous amount of research into this area in the past decade.[6, 22, 25] Even though, dispersion in certain solvents has been achieved through sonication, precipitation occurs immediately the sonication is stopped. However, the interaction of carbon nanotubes with certain classes of compounds to form supramolecular complexes allows them to be easily fabricated towards applications in innovative nanodevices.[6]

Chemical manipulation of pristine carbon nanotubes dramatically improves solubility which allows them to be easily incorporated into organic, inorganic and biological systems.[6,26] In general three main approaches to chemical and structural modification of pristine carbon nanotubes have been reported.[6] These are:

a) Covalent bonding to other chemical groups

b) Noncovalent adsorption / wrapping of various functional molecules

c) Filling of the inner empty cavities

Basically, the tubes are made of an assembly of carbon atoms in a hexagon arranged helically around the axis of the tube with varying pitch for each concentric tube.[4,18]

Current methods use in the synthesis of both SWNTs and MWNTs include carbon-arc discharge, laser vaporization, chemical vapor deposition, electrochemical methods, pyrolytic methods.[9,19,20,23-24]

There are two basic forms of carbon nanotubes that have been identified and characterized by various authors.

These are single-walled nanotubes (SWNTs) which are made up of a single sheet of carbon atoms seamlessly joined together to form a tube having a cylindrical shape. The other is a multi-walled nanotube (MWNT) which is basically an assembly of the SWNTs within each other giving rise to concentric rings of carbon sheets.[4,7] However this description of the MWNTs by Iijima[8] has been challenged by the work of David et al. where electron microscopy were used to study the detailed network of the MWNTs[9] which has been collaborated by other authors.[18] They are usually capped at the two ends by a hemisphere-like fullerene cap made up of pentagonal carbon rings.[4]

1.3: PROPERTIES OF CARBON NANOTUBES

1.3.1: Electronic Property

Carbon nanotubes have been found to be either metallic or semiconductors depending on the helicity of the tube and tube diameter. The helicity or direction of fold of the skeletal carbon network in the direction of the tube growth is determined by a pair of integers (**n, m**) which differentiate one conformer from the other.[7,18] There are three types of identifiable tubes with different properties based on the above classification.[7,10]

These are:

(a) Armchair, where n = m e.g. (10,10)

(b) Zigzag, where n = 0 or m = 0 e.g. (0,10)

(c) Chiral where n, m = combinations of all integers except as in (a) and (b) above

The above identifiable conformations impart unique electronic properties to the tubes. The armchair conformer are all metallic, however, those with n-m = 3k, where k is a non-zero integer, are semi-conductors having small band gap. All other combinations except the above are semiconductors having a band gap that depends on tube diameter.[7]

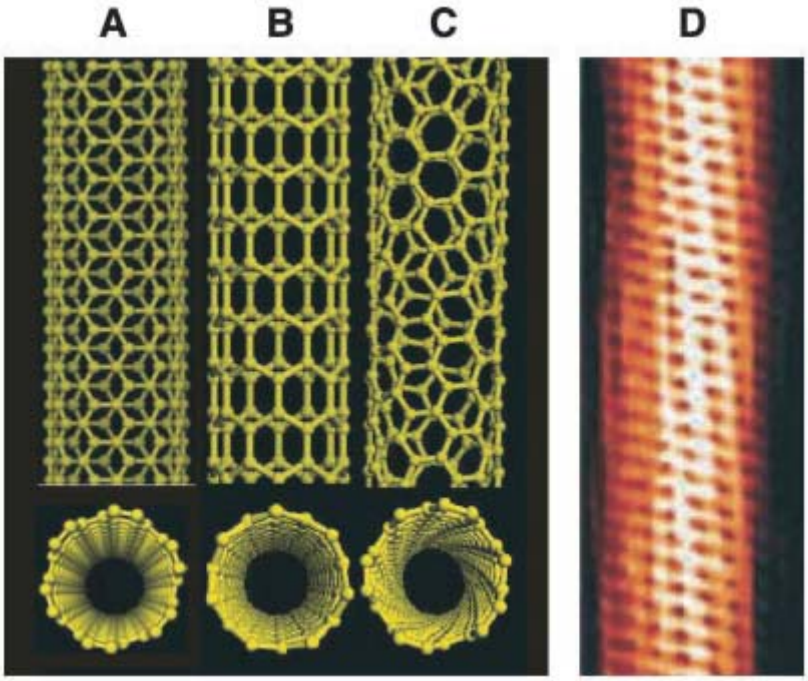


Figure 1.2: Schematic representation of different conformations of single-walled tubes (A) arm-chair configuration, (B) Zigzag configuration, (C) Chiral configuration, (D) TEM image of 1.3 nm diameter chiral SWNT[7]

Metallic and defect-free SWNTs are able to carry high currents and conduct electricity with minimal heating with no resistance at room temperature due to the ballistic nature of electron transport within the tubes.[7] Electrons move freely and unimpeded in the tube with no scattering from atoms/tube defects.[7, 10, 17]. They also have high thermal conductivity of 3000W/mK, which is higher than that of diamond and graphite (2000W/mK). In certain instances superconductivity has been observed at low temperatures.[7]

1.3.2: Mechanical Property

Both SWNTs and MWNTs are known to be stiff and strong with desirable Young's modulus (~0.64 TPa) and tensile strength.[7]

The defect-free SWNT bundle ropes can extend their length elastically by 5.8 % before breaking. This implies the strength of such rope is estimated to be around 37 GPa which is as close as the highest strength attainable in a silicon carbide rod.[7]

Perfectly defect-free pyrolytic carbon nanotubes have Young's modulus of ~1.06 TPa which is far higher than the 0.66 TPa of silicon carbide nano fibers.[7] This means their "Density-normalized modulus" and strength are ~19 and ~56 times higher than steel wire and ~2.4 and ~1.7 times higher than silicon carbide rod.[7]

This enormous inherent strength coupled with their light weight makes them useful in various applications that require light materials without compromising on strength.[7]

1.4: THEORETICAL DISCUSSION OF THE STRUCTURE OF CARBON NANOTUBES

A pristine, defect-free carbon nanotube has a translational unit cell along the axis of the tube in a cylindrical form. Most of the physical and electronic properties of a particular tube, defined by a set of integers (***n, m***) can be gleaned from the unrolled version of this cylindrical unit cell. A unique integer set determines certain basic characteristics of a particular tube such as diameter, length, helicity and electrical properties.[18] For a given set of integers (n, m), if n = m, the tube tends to be metallic, however, when n – m is a multiple of 3, the carbon nanotube is semiconducting with a small band gap. All others trends to have a moderate semiconducting properties. Also for given set of integers (n, m), if n = m, the nanotube is said to have an armchair configuration. In a situation where m = 0, the nanotube has a zigzag configuration. For all other combinations, the tube is said to be chiral.[7]

In its simplest form, the structure of a carbon nanotube can be specified uniquely by a vector, **C** which connects any two equivalent points on the two-dimensional graphene sheet.[2] Each set of integer represents a unique structure and is related to the vector **C** as:

$\mathbf{C = na_1 + na_2}$, where $\mathbf{a_1}$, $\mathbf{a_2}$ = unit cell base vectors of the graphene sheet (Figure 1.3).

For a typical armchair carbon nanotube, the magnitude of $\mathbf{a_1 = a_2 = 0.246\ nm.}$ Thus the magnitude of C is given by[2]:

$$C = 0.246(n^2 + nm + m^2)^{1/2}$$

And the diameter d_t of the tube is given as[2]:

$$d_t = 0.246\{(n2 + nm + m2)/\pi\}^{1/2}$$

For an armchair configuration, the width of a unit cell, w_t is given as the magnitude of **a**.

$w_t = |\mathbf{a}|$, where **a**= unit cell base vector of the graphene sheet.[2]

In the case for a zigzag carbon nanotube,

$W_t = |(3a)^{1/2}|$

The length of a unit cell of carbon nanotube in the direction of the tube axis is the magnitude of the vector T, which can be derived from the vector C and the set of integers (n, m) defining such a particular tube[2], where;

$|T| = (3C/d_H)^{1/2}$, if $n-m \neq 3rd_H$ or

$|T| = (3C/3d_H)^{1/2}$, if $n-m = 3rd_H$; d_H = highest common divisor of n and m; r = some integer

Similarly, the number of carbon atoms in a unit cell of a tube defined by a set of integers (n, m) is given by 2N, where:

$N = 2(n^2 + m^2 + nm)/d_H$; if $n-m \neq 3rd_H$ and

$N = 2(n^2 + m^2 + nm)/3d_H$; if $n-m = 3rd_H$

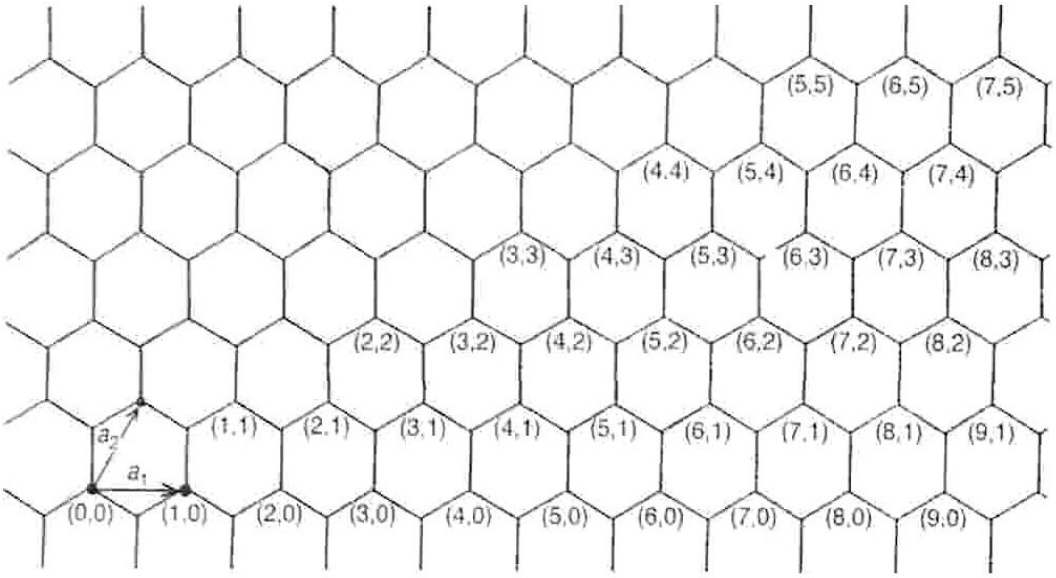


Figure 1.3.Unit vector of 2D lattice of graphene layer with labeled atoms using (n, m) nomenclature[2]

1.5: CURRENT PRODUCTION METHODS FOR CARBON NANOTUBES

There are basically two general approaches to the synthesis of carbon nanotubes. Catalytic and non-catalytic methods have been used to varying degree of success with each having its own advantages and disadvantages. Employing any of these approaches depends on what kind of carbon nanotubes one desires. The main criteria to be considered are:

i) Type of nanotube, i.e. MWNT or SWNT

ii) Purity of tubes desired.

iii) Level of defect.

iv) Yield levels desired.

Notwithstanding, any of the above approaches employs four main techniques to produce the carbon nanotubes.[7, 8] They are:

i) Arc discharge technique (AD)

ii) Laser ablation (LA)

iii) Chemical vapor deposition (CVD)

iv) High pressure CO conversion

1.5.1: Arc Discharge Method

This method relies on the creation of carbon vapor between two carbon electrodes by an arc discharge. Subsequent deposition of such carbon vapors self assemble to form the tubes. Pure carbon electrodes produce MWNTs alongside a lot of other contaminants such as fullerenes, amorphous carbon, and graphitic carbon sheets and fragments.[12] Tubes produced this way always require some level of purification which can result in damage to the tubes.[21] However the absence of heavy metal catalyst in this process eliminates the need for acid purification which usually compromises the morphological integrity of the tubes. When SWNTs are desired, the carbon electrodes must be doped with metal catalyst such as Fe, Co, Ni, Y or Mo in addition to the platinum-group metals.[28] Mixtures of metal dopants have also be used giving rise to varying degree of purity and defect. In both cases the quantity and quality of tubes produces depends on many operational factors and parameters of the set-up.[28]

These include the kind of inert gas employed, the pressure of the inert gas within the chamber, the amount of current applied and the general geometry of setup in the arc, e.g. the distance between the cathode and the anode.

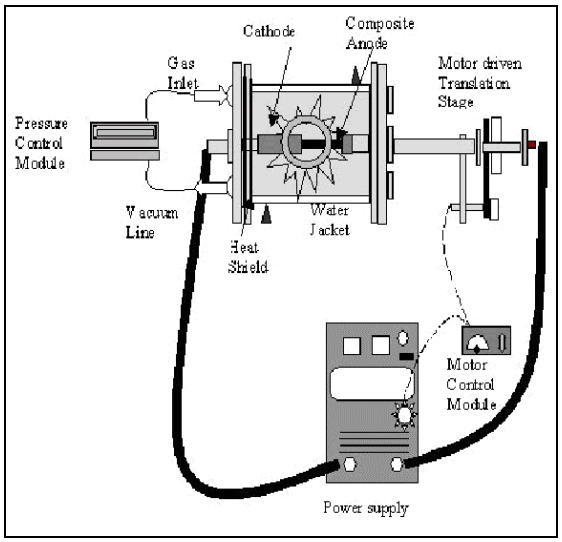


Figure 1.4. Schematic illustration of arc-evaporation apparatus for the for the production of carbon nanotubes

A typical set up for the synthesis of carbon nanotubes is as shown in Figure 1.4. This is a modification of the original set-up used by Iijima and was developed by Ebbesen and Ajayan. This modification made the realization of gram scale synthesis of the tubes a reality and made available macroscopic quantities of carbon nanotubes for the first time.[12]

Description[2, 28]

Chamber is connected to a helium supply (inert gas) and a pump

Two graphite rods of high purity having unequal lengths ($A_L > C_L$, D_A = 6mm, D_C = 9mm)

A water cooling system

DC-voltage source, Voltage = 18 V with a current output of 50-100 A

An optimal pressure of 500 torr

Usually set-up is enclosed in a fume-hood.

Mode of operation[2,12,28]

The helium is opened to fill the chamber after which the pump is put on to generate a continuous flow of the inert gas resulting in stabilized pressure. The adjustable graphite rod is controlled from outside the chamber to create a gap/separation between the two anodes during operation and arcing. A stabilizing Dc-voltage of approximately 20 V is then applied. When the

current is turned on, the adjustable anode is then moved closer to the cathode slowly until an optimum gap separation for arcing to occur. This gap is maintained by constantly adjusting the anode from outside throughout the arcing process (~1mm or less). Under these conditions the rod is consumed at a rate of few millimeters per minute.

After consumption of rod, power is turned off and the chamber is left to cool.[2, 12-13] The cathode rod with its deposits is then removed and analyzed to recover the nanotubes formed. Figure 1.5 shows a cross-section of a rod-shaped deposit with the cathode on which it forms.[12]

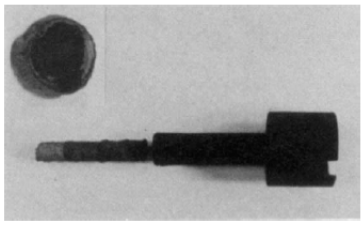


Figure 1.5. Rod shaped deposit with the larger graphite rod on which it forms[12]

Upon examination using transmission electron microscopy (TEM), two easily separable distinct layers consisting of an inner black central core and an outer gray hard shell were found. The outer layer was metallic in nature with no nanotubes present whilst the inner black layer was made of nanotubes and particles. The yield was 25% with a tube – particle ratio of 2 by weight. This was further purified by agitation in an ultrasonic bath.[12]

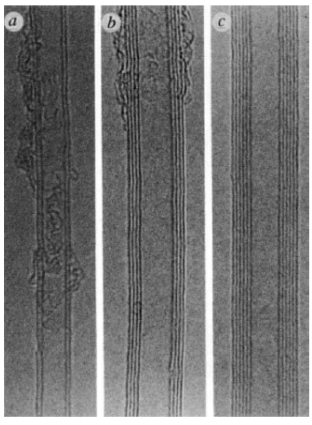


Figure 1.6. High resolution electron micrographs of typical MWNTs showing a distance of ~0.34 nm between concentric tubes[12]

1.5.2: LASER ABLATION METHOD

This procedure like the arc-discharge method, involves vaporization of carbon. However, a laser beam is rather employed to impinge on a graphite rod in an oven maintained at 1200^{o}C. A continuous or pulsed laser beam has effectively been used in this process. This approach was first used by Smalley et al. in 1995 to produce very high yields of purer virtually defect-free SWNTs with uniform sizes in diameter.[14] Like the arc-discharge method, use of pure graphite rods results in MWNTs whilst graphite rods doped with heavy metals produces SWNTs. Such SWNTs are usually bundled together as ropes which are held together by van der Waals forces of attraction. Successful scale up of this method will surely led to macroscopic amount of highly pure desire single walled carbon nanotubes for various applications and intense research is currently being conducted by various researchers in this direction.[14]

1.5.3. CHEMICAL VAPOR DEPOSITION

In this method, gaseous hydrocarbons and other carbon source gases such as methane, carbon monoxide, or acetylene are heated by high temperature plasma or coils between 650^{o}C ~ 900^{o}C in a gas phase.[33] Such high temperatures produce reactive atomic carbon. These atomic carbon species diffuse to a catalyst coated substrate/ support where the carbon nanotubes are formed upon cooling. This method preferentially gives SWNTs if the appropriate metal catalyst is employed. The catalysts usually employed are transition metals such as Ni, Fe or Co[31- 32] or the platinum-group metals. In addition better control of tube diameter and rate of deposition can be achieved by maintaining optimal parameter.[29, 31-32] In general this process may be divided into two main steps.[33]

These are: i) catalyst preparation into extremely fine particles and their subsequent deposition and nucleation on a substrate/support by either chemical etching or thermal annealation, ii) Tube growth as the reactive atomic carbon get deposited in the catalyst coated substrate. Even though yield of tubes by using this methods are characteristics low (typically 30%), it results in much purer, mostly SWNTs.[33]

1.6. PURIFICATION OF CARBON NANOTUBES

Production of carbon nanotubes in high purity and yield remains two of the biggest challenges to researchers and material scientist in this field.[33] In this direction, new methods and optimization of existing ones are continuously being explored and reviewed. However, until such a novel method producing such highly pure carbon nanotubes is found, existing purification processes will continue to be the only plausible alternative in realizing pristine carbon nanotubes at the level of one desires for use in any potential application.

The impurities usually associated with freshly produced carbon nanotubes depending on the technique employed includes but not limited to fragmented graphite sheets, amorphous carbon, metal catalyst, and smaller bucky balls.[33] To adopt the tubes to any application of studies, these impurities must be removed to avoid or minimize their possible interference with the desired or measured properties. At the same time, preserving the integrity of the tubes is crucial in these purification processes. However, most of the current methods fall short of this criterion.[25, 27] Among them are:

i) Strong acid oxidation of organic impurities

ii) Metal catalyst removal by acid treatment

iii) Annealing

iv) Ultrasonication

v) Magnetic treatment

vi) Micro filtration

vii) Cutting

viii) Chemical functionalization

ix) Chromatography

Most of these methods do some amount of damage to the tubes in addition to removing the undesired debris. Such damages range from tube oxidation in the case of acid treatment to cutting them up.[25-27] In addition, most of these purification processes are cumbersome and can add to the overall cost of production of the tubes. In most instances, for practical purposes, several of the above-mentioned techniques must be combined in series to acquire the highly desired pure pristine carbon nanotubes.

1.7. USES AND POTENTIAL APPLICATIONS OF CARBON NANOTUBES

Many authors and researchers have proposed a lot of potential applications for carbon nanotubes and nanoparticles both in research and in industry since its discovery.

Even though most of these so-called potential applications still remain mere speculation, some have successfully been proven experimentally whilst few have made it to the commercialization stage.[25] Among the possible potential uses to which these materials can be put are listed below: [7, 33]

Conductive and high strength reinforcement composites.

Energy storage devices[7]

Energy conversion devices[42]

Sensors and probes[39]

Field emission and radiation source devices

Conductors and semiconductors[41]

Nano interconnects in electronic devices[41]

Super nanomagnets and "nanowires"

Means of effective vehicular delivery of drugs to targeted organs.[34 - 38]

1.7.1. Carbon Nanotube composites

Development of molecular composites to give strength and versatility in function and uses to materials such as plastics (polymers), ceramics, and metals have captured the imagination of material scientist since the dawn of the industrial revolution.[33, 40] Certain carbon fibers despite their structural imperfections have been utilized in this direction in many products ranging from golf clubs to military aircrafts.[2]

It was therefore not surprising when carbon nanotubes hit the headlines in most scientific journals in the early 1990s, with its exceptional strength and conductive properties attention was drawn to these novel materials to be used as reinforcement composites.[4]

Many experiments have confirmed individual SWNTs to be overwhelmingly stiffer than the conventional carbon fibers used as reinforcement composites and more so than any known material. They have less defects in their structure and their strong sp^2 carbon-carbon bonds with very small bond distances makes it possible to exclude most impurities from their basic structure

thus giving them high tensile strength.[14] Use of nanotube composites as electrically conducting materials was one of the first major commercial application of these novel materials.[7]

Loading levels of 5% and below in plastics has been reported to achieve reasonable conductivities to avoid electrostatic charge build-up in automobile gas cylinders and filters. It also maintains the integrity of these gas lines and filters making them more resistant to tear and wear and also prevent fuel diffusion through them.[7]

Plastic semi-conductor chip carriers, reading heads, and conductive automotive parts are few of the products that have been fabricated using carbon nanotubes as composite reinforcement and are currently in commercial use. Others include SWNTs and MWNTs composite plastics being employed in the shielding of electromagnetic radiation from cell phones and computers in addition to imparting high strength and stiffness to the material.[7, 15, 33]

Work by Biercuk et al. indicated that 2% loading of SWNT into plastics lead to three and half fold increase in resistance to rupture with an additional two-fold increase in thermal conductivity. Also polystyrene doped with 1% MWNT enhanced drastically the modulus and breaking stress by 42% and 25% respectively.[7]

One technical problem in this area is how to effectively disperse the nanotubes uniformly within the matrix to avoid sliding between tubes in SWNT bundles and between concentric layers in MWNT. In summary, carbon nanotubes reinforcement increases toughness as a result of its ability to absorb energy and their elastic behavior. In addition the low density of the tubes coupled with their impressive electrical conduction results in better performance of composites when subjected to compressive load.[33]

1.7.2. Energy storage Devices

Carbon nanotubes also have useful application in the fabrication of electrodes for nano-electronic devices that require the use of "electrochemical double-layer charge injection" for higher power output.[7, 33] These include "supercapacitors", electrochemical actuators.[16]

Electrochemical capacitors based on carbon nanotubes give higher capacitance than ordinary dielectric capacitors even upon application of small amount of voltage (~10V) compared to ~100 to 1000V and over for piezoelectric stacks and electrostatic actuators respectively.[7]

Output capacitance in these devices is directly related to charge per unit area on the carbon nanotube and the counter charge in the electrolyte unlike ordinary capacitors which has a reciprocal relationship to the inter-electrode distance which are usually at the micrometer scale at best.[33] Thus the small nano size of the carbon tube electrodes coupled with the high charge it can carry makes them excellent energy storage devices which can be applied in electronic devices that require higher power output than ordinary batteries and the conventional capacitors can provide.[7,33]

In summary, carbon nanotube-based electrochemical capacitors are very much desirable due to their:

- Capacitance output/higher charge storage
- Higher power densities
- Shorter discharge time
- Low operating voltage
- Large range of operational temperature even up to a 1000^{o}C

Other promising areas of application in the area of energy storage include hydrogen fuel cells and rechargeable lithium ion batteries. Carbon nanotubes have the ability to store liquid or gaseous materials in their inner cavities through a capillary effect. They have been found to exceed the 6.5% by weight threshold requirement by the US Department of Energy for effective commercial utilization of any material to be used for hydrogen fuel cells. Notwithstanding, detailed mechanism of the storage is yet to be fully explored.[33] Lithium battery cells operate on the principle of electrochemical intercalation and de-intercalation of lithium in the electrodes employed. Lithium has the highest point saturation in carbon nanotubes due to its enormous ability to fill all the interstitial sites available in carbon nanotubes.[33]

1.7.3: Field Emission Devices

Work on the use of SWNTs and MWNTs as field emission electron source for use in flat panel displays, lamps, gas discharge tubes, X-ray, microwave generators have all been explored by various researchers.[7,33]

The advantages of these devices over the conventional metals like tungsten and molybdenum are:

- relatively easy manufacturing /fabrication process
- less deterioration in moderate vacuum (10^{-8} torr)
- provision of more stable emission
- long life times
- high current densities of ~ 4A/cm^2

Other desirable properties that make carbon nanotubes promising materials as field emitters are their nano size diameter, structural integrity, high electrical conductivity, small energy spread and high chemical stability.[33]

Notwithstanding these favorable advantages carbon nanotube-based emission devices faces stiff competition from liquid crystals panel display and other organic and polymeric light-emitting diode displays.[7]

Studies on a field-effect transistor made from a semi-conducting SWNT by Baughman et al, have been shown to have the ability to be switched from conducting to an insulating state. A logical switch, the basic components of computers can be constructed from such carbon nanotube transistors when coupled to each other.[7, 33]

1.7.4. Nanometer-Sized Electronic Devices

Other areas of application worthy of consideration include nanometer-sized electronic devices where SWNTs and MWNTs have been noted to be useful in fabrication of electronic circuits so small in size yet maintain or even improve the current "computational power" of circuits.[33] Experimental results in this area have proved very positive and promising but more research is needed in this direction to achieve this objective.[7, 17, 33]

Conventional metal wire interconnections in electronic circuits have been reported to fail when the wire size is reduced beyond a certain threshold minimum at the micrometer scale[7]. This makes carbon nano wires the future conductors in circuits in the ever shrinking sizes of electronic devices required for various applications and other lightweight electrical consumer products as more consumers continue to fancy such small appliances. This area has been made bright by the fact that molten metals like lead and copper have been drawn into opened carbon nanotubes by capillary action to form nano wires with excellent and improved conductivity.[2]

1.7.5. Nanoprobes and Sensors

Fabrication of the cantilever tips of AFM and STM instruments from carbon nanotubes is expected to result in crash-proof operation and higher resolutions of images. This is made possible due to their nano size diameters, high electrical conductivity; high elasticity and strength.[33] The currently available silicon and metal tips do not offer all these desirable properties, thus requiring careful and expensive fabrication processes only to produce fragile tips.

1.8: CONCLUSION

Carbon nanotubes continue to engage the attention of researchers and the business community since its discovery almost a couple of decades ago. They come in two main forms which can be either a multi-walled carbon nanotube (MWNT) or a single-walled carbon nanotube (SWNT). Electronically, it may behave as metal or a semi-conductor depending on a special conformation adopted which are defined by a set of integers (**n, m**). Amidst this fascination, the potential applications of these novel carbon materials continue to expand. They have superb electronic and mechanical properties that position them to be the material of choice for the next century. They are known to have desirable properties that can be useful in the design and fabrication of nano electronic devices, composite reinforced materials and drug delivery in biological systems.

CHAPTER 2 - SYNTHESIS OF [12, 12] CARBON NANOTUBE VIA A FERROCENYL INTERMEDIATE

2.1: Introduction and Background

Since their discovery in 1991 carbon nanotubes has attracted the attention of many professionals especially in material science and continues to fascinate researchers in nanotechnology. The volume of proposals into their potential applications has been propounded by experts both in research and in industry and continues to expand daily.[6] These applications ranges from conductive and reinforcement component materials in composites to nano interconnection in electronic devices. Other applications potential applications include but not limited to biosensors and probes to drug delivery.

However, current methods of production results in tubes which are impure and highly heterogenous in length, diameter, and chirality. Consequently mixtures of tubes which are either metallic or semiconducting are formed. To effectively apply such carbon nanotubes to use, they must be thoroughly purified and sorted out into like forms. Current purification methods are cumbersome and are usually performed under harsh conditions. This eventually compromised the integrity of the tubes thus reducing their potential uses and effectiveness.

Also carbon nanotubes produced by these traditional methods are mostly insoluble in most solvents. Increased solubility in basic organic solvents is crucial prior to applying them to any meaningful use. This requires some level of chemical manipulation or functionalization on the tubes. Currently most methods of functionalization are unpredictable and limited to few oxidation reactions. Precise derivatization of carbon nanotubes is required for application in drug delivery.

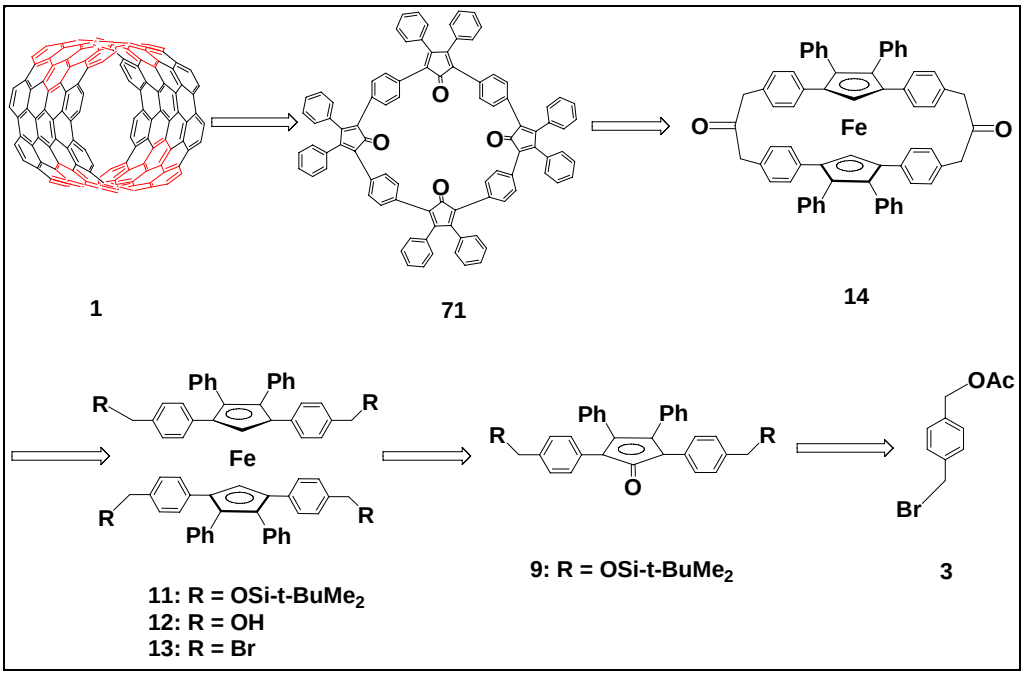
There are no such precise methods currently available to realize highly pure, functionalized carbon nanotubes with predetermined length and diameter. This greatly undermines the realization of these valuable materials in consumer products as quickly as expected considering its enormous applications in material science.

A rational synthetic approach to make single-walled carbon nanotubes (SWNTs) with predefined diameter and length with the possibility of incorporating desired functional groups in the course of production was investigated. Protocol relying on classical chemical synthetic approach was used and results achieved so far will be presented in this dissertation. Such an approach is expected to address most if not all of the problems associated with the traditional methods of producing carbon nanotubes.

2.2: Retro-synthesis

The retro-synthetic scheme to synthesize an arm-chair [12, 12] SWNT by employing a rational synthetic approach is shown in Scheme 2.1 below.

Scheme 2.1. Retro-synthetic analysis of [12, 12] single-walled carbon nanotube



A belt-like intermediate **72** will be used to synthesize an all phenyl substituted macrocyclic paracyclophane **32** which will subsequently be converted to the target SWNT **1** by oxidative dehydrogenation with ferric chloride in nitromethane.[43] Intermediate **72** will be synthesized from a Knoevanagel-type condensation of **14** with benzil. In order to avoid producing different kinds of oligomers during the formation of the macrocyclic intermediate **14**,

iron is used as an anchor in the form of a ferrocene with the desired substitution to effectively close the ring. This makes the acyclic and macrocyclic ferrocenyl intermediates **11** and **13** very crucial in the overall synthetic effort (Scheme 2.1). Compound **11** will be synthesized from the cyclopentadienone **9** which will be synthesized from 4-(Bromomethyl)benzyl acetate **3** by carbonylative coupling reaction mediated by iron pentacarbonyl and subsequent condensation with benzil. The intermediate **3** will be synthesized from 1,4-Bis(bromomethyl)benzene **2** derived from radical bromination of the two methyl groups of *p*-xylene using *N*-bromosuccinimide (NBS) and peroxide (Scheme 2.2).

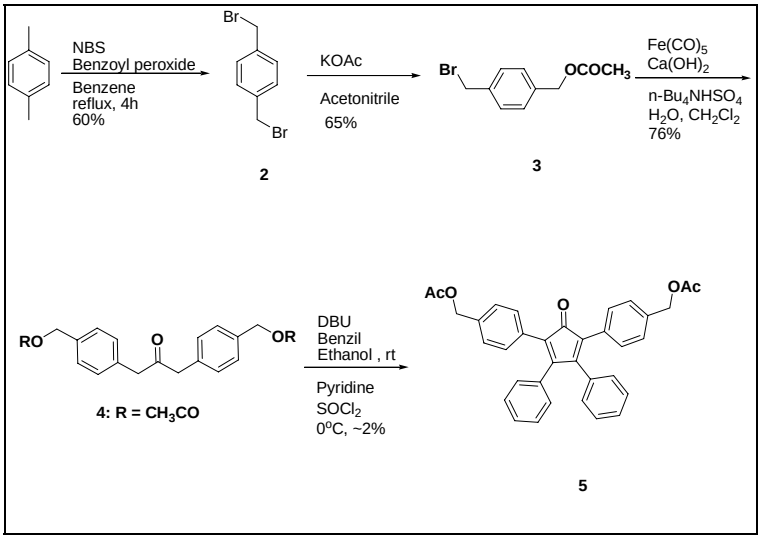
2.3. Synthesis

2.3.1. Synthesis of Acyclic Ferrocene Intermediate 2.11

Dibromide **2** was prepared by radical bromination of the two benzyl positions in *p*-xylene using *N*-bromosuccinimide in 60% yield. Benzoyl peroxide was used as a radical initiator for the bromination reaction.[44]

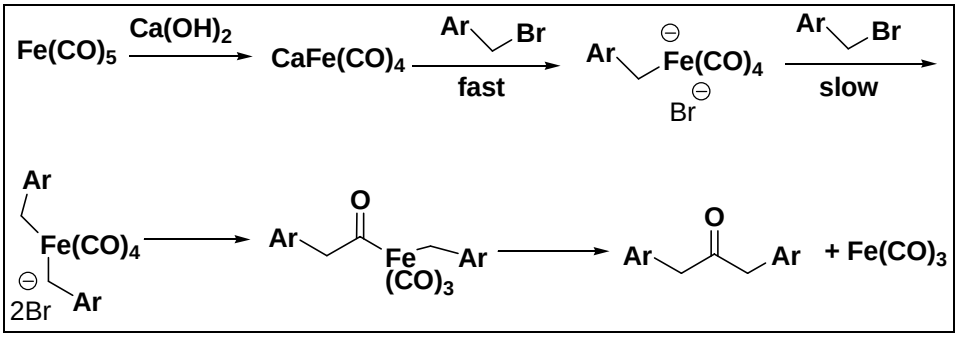
Bromomethylbenzyl acetate **2.3** was synthesized from **2.2** following a slight modification of the procedure reported by Diederich et al. in 65% yield using potassium acetate (KOAc) in acetonitrile (CH_3CN).[45]

Scheme 2.2: Synthesis of cyclopentadienone 5



Carbonylative coupling reaction of the bromide mediated by $Fe(CO)_5$ in dichloromethane and water at room temperature with a phase transfer catalyst gave the symmetrical ketone **2.4**.[47-48] in 76% yield. The reactive agent in the carbonylative coupling is believed to be a calcium salt of iron tetracarbonyl where the iron is in -2 oxidation state. According to Hughes et al, the proposed mechanism for the carbonylative coupling involves two oxidative additions with the first being much faster than the second as shown in Scheme 2.3.[47]

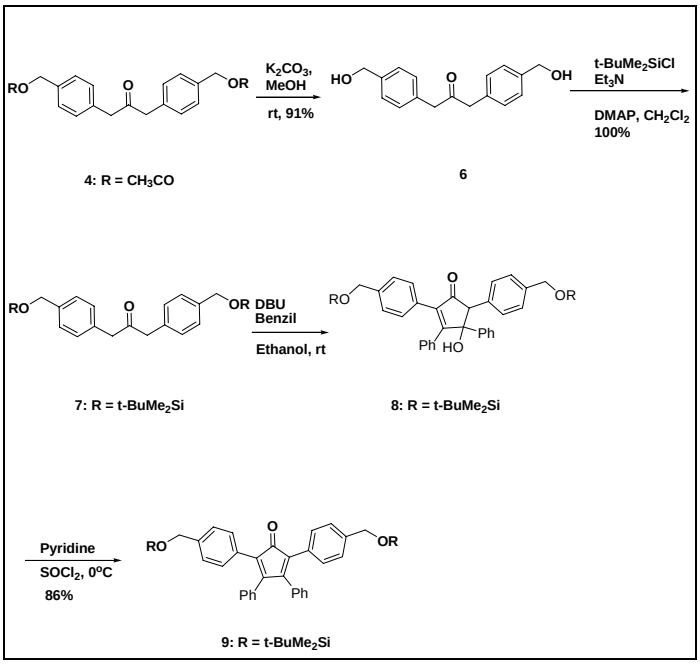
Scheme 2.3: Proposed mechanism for the carbonylative coupling of benzyl bromide



The symmetrical acetate-protected ketone **4** was subjected to an aldol condensation reaction with benzil and 1,8-diazabicyclo[5.4.0]undec-7-ene.[48] Surprisingly, only trace amount of the cyclopentadienone **5** was observed (Scheme 2.2). The acetate moiety did not survive under the prevailing basic reaction condition. A highly polar material was obtained which was difficult to purify by column chromatography and could not be fully characterized. It was therefore decided to replace the acetate with a substituent that is more likely to withstand the prevailing basic reaction conditions.

The acetate was therefore removed from intermediate **4** with potassium carbonate in methanol to give a symmetrical di-ol, **6.** This was further protected with *t*-butyldimethylsilyl chloride (TBDMS), triethylamine and 4-(dimethylamino)pyridine (DMAP) in methylene chloride as shown in Scheme 2.4.

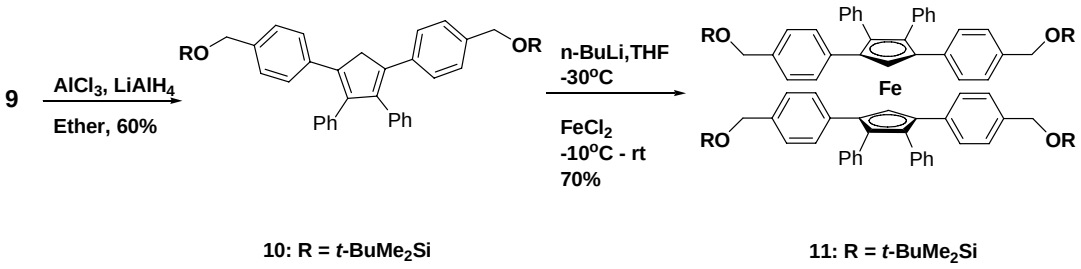
Scheme 2.4: Synthesis of silyl-protected cyclopentadienone 9



The silyl-protected di-ol was subjected to an aldol condensation with benzil and DBU in ethanol at room temperature.[48] The Aldol-adduct was expected to fully dehydrate to give the condensation product **9**. However, a mixture of the condensation product and the incomplete dehydrated intermediate alcohol **8** were formed. Consequently, this crude mixture was further treated with thionyl chloride and pyridine to complete the dehydration process to give the cyclopentadienone **9** in overall 86% yield from **7**.[48]

The carbonyl functionality in the cyclopentadienone **9** was reduced with aluminium hydride generated in situ with aluminium trichloride ($AlCl_3$) and lithium aluminium hydride ($LiAlH_4$) in diethylether to afford the cyclopentadiene **10** in 60% yield[49] as presented in Scheme 2.5.

Scheme 2.5: Synthesis of acyclic ferrocene intermediate 11



This was converted into an acyclic ferrocenyl intermediate **11** in 70% yield by treatment with n-BuLi in THF and iron (II) chloride ($FeCl_2$). The ferrocene is expected to serve as critical intermediate in the construction of the macrocyclic molecule which will later be converted into a carbon nanotube having pre-defined diameter, length and incorporation of appropriate desired functionality through a series of chemical reactions. The pre-defined parameters of the resulting carbon nanotube will depend on the size of the initial macrocyclic ferrocene. The iron in the ferrocene is expected to act as an anchor in a ring closing reaction thus minimizing any unwanted oligomers and by-products.[49] The structure of **11** was unequivocally determined by a single – crystal analysis (Figure 2.1)

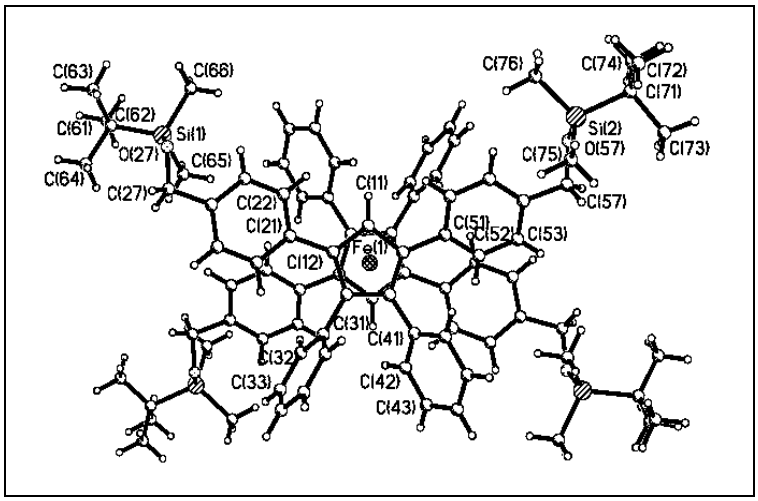


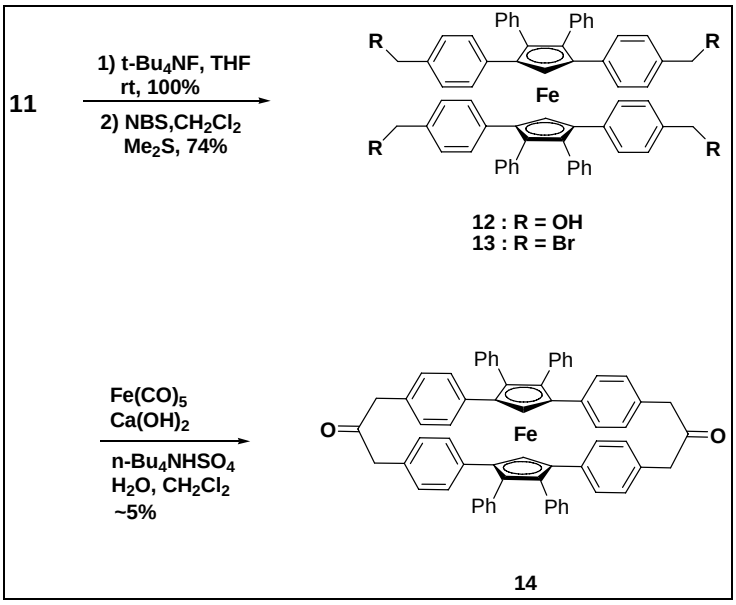
Figure 2.1: Single-crystal X-ray analysis of acyclic ferrocene 11

2.3.2: Synthesis of the Ferrocenophane 2.14

Desilylation of the of ferrocene **11** with tetrabutylammonium fluoride (TBAF) in THF gave the ferrocenyl alcohol **12** which was brominated with excess NBS and dimethylsulfide in methylene chloride to give the tetrabromide **13** in 74% yield**.** Exhaustive bromination of **12** was also achieved by treatment with PPh_3-CBr_4 in methylene chloride. Employing a similar carbonylative coupling method used by Hughes et al.[47] to synthesize various ketones from benzyl halides, **13** was expected to be easily converted to ferrocenophane **14** without much difficulty.

Consequently the bromide was treated with $Fe(CO)_5$, $Ca(OH)_2$ and n-Bu_4NHSO_4 in a two phase reaction using water and methylene chloride as presented in Scheme 2.6.

Scheme 2.6: Synthesis of ferrocenophane 14

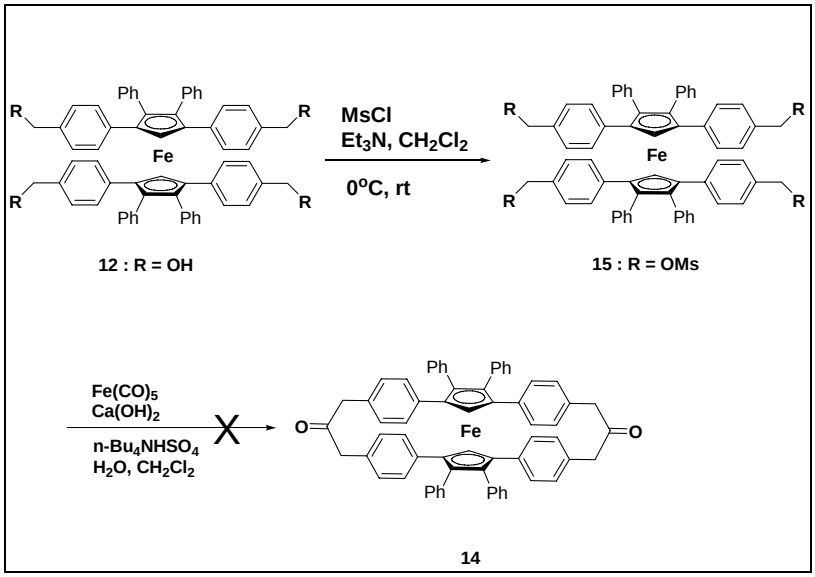


There was evidence of the desired product **14** (up to 5% yield) from this reaction. The yield was unexpectedly low with many side products. It was realized that the success of this reaction also depends on keeping all the four benzyl bromines intact. Losing any one of them in the course of the reaction will lead to failure in the ring closing carbonylative coupling reaction.

Under such basic conditions, the bromine could easily be hydrolysed to an alcohol since it is such a good leaving group. Such hydroxyl functionality could easily interact with an adjacent benzyl bromide to form ether. Such cyclized ethers and their un-cyclized derivatives were observed by mass spectrometry in addition to some other unidentifiable materials which were not characterized further.

The carbonylative cyclization was also attempted with tetramesylate **15** which was obtained by treating alcohol **12** with triethylamine and methanesulfonyl chloride in methylene chloride (Scheme 2.7). However, this approach was not much different from using the tetrabromide and resulted in unidentifiable side products which were not further characterized.

Scheme 2.7: An alternative route to the ferrocenophane 14



1.3.3. Synthesis of the Tetrahydroxyferrocenyl Cyclophane 2.18

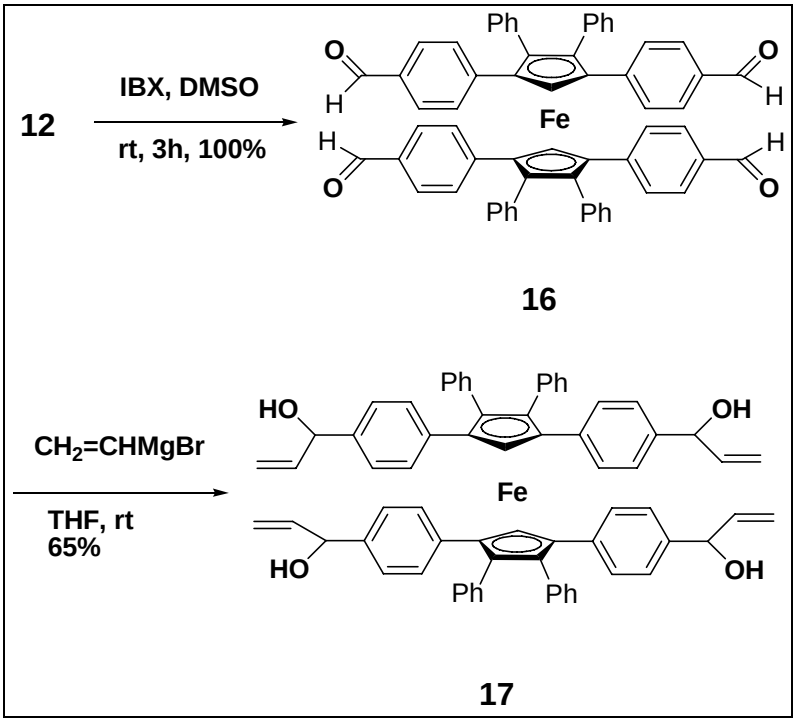
At this point an alternative synthetic pathway was envisaged and employed to construct the target carbon nanotube **1**. It was proposed that if the strain during the cyclization could be relieved by lengthening the linker, the cyclization could proceed effectively with improve yield. To avoid a significant shift in the original idea, a new protocol was found to add an additional carbon to the original intermediates prior to the cyclization step.

A versatile and commonly used carbon-carbon bond formation by Grignard was selected as an ideal way to go. In addition to that, incorporation of terminal alkene functionality will allow the formation of the critical initial macrocyclic ring by alkene metathesis. This was expected to pave the way for further chemical elaboration to synthesize the target compound **1**.

The acyclic ferrocenyl tetraol **12** was oxidized completely with *o*-iodoxybenzoic acid (IBX) in DMSO to form tetraformyl ferrocene **16.** This was subjected to Grignard reaction with 6 eqv of vinyl magnesium bromide in THF at room temperature to obtain compound **17** in 65%

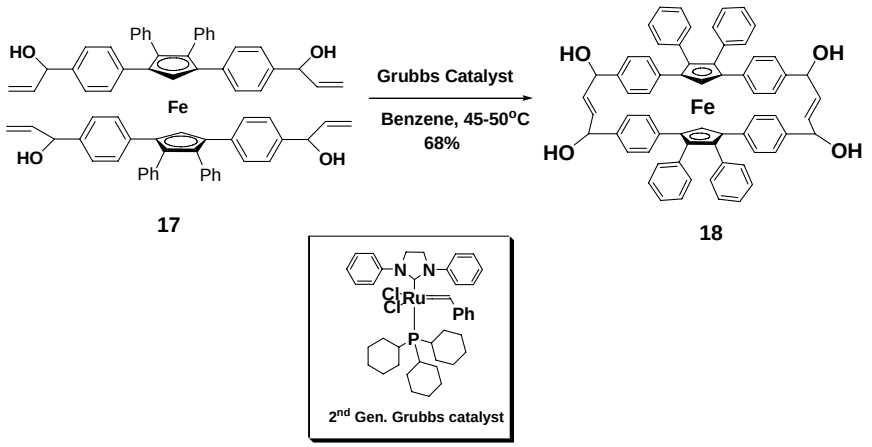
yield. The incorporation of the terminal alkenes in **17** allowed the construction of the macrocyclic ferrocenylcyclophane through a facile ring closing metathesis (RCM).

Scheme 2.8. Synthesis of the acyclic ferrocene 17



The macrocyclic product was also expected to be less strain due the incorporation of an additional carbon in each linker. The tetraene **17** was subjected to a second generation Grubbs catalyst in benzene in high dilution (10^{-4} M) at 50^{0}C to give **18** in 68% yield as shown in Scheme 2.9.

Scheme 2.9. Synthesis tetrahydroxy ferrocenophane 18



Due to the high volume of benzene involved, it become necessary to recover the benzene by distillation for re-use. Failure to conduct the reaction under such high dilution resulted in the dimerized (**19**), trimerized (**20**) and in some cases the tetramerized (**21**) macrocyclic products in addition to the cyclized monomer (Figure 2.2). This eventually led to low yields of the monomer. However, it should be noted that formation of the monoferrocenophane, the diferrocenocyclophane and the higher analogues will serve as key intermediates for the construction of the carbon nanotube **1** and its analogues having larger diameter tubes. Also in certain instances incomplete cyclization was observed for some of the higher analogues of the ferrocene.

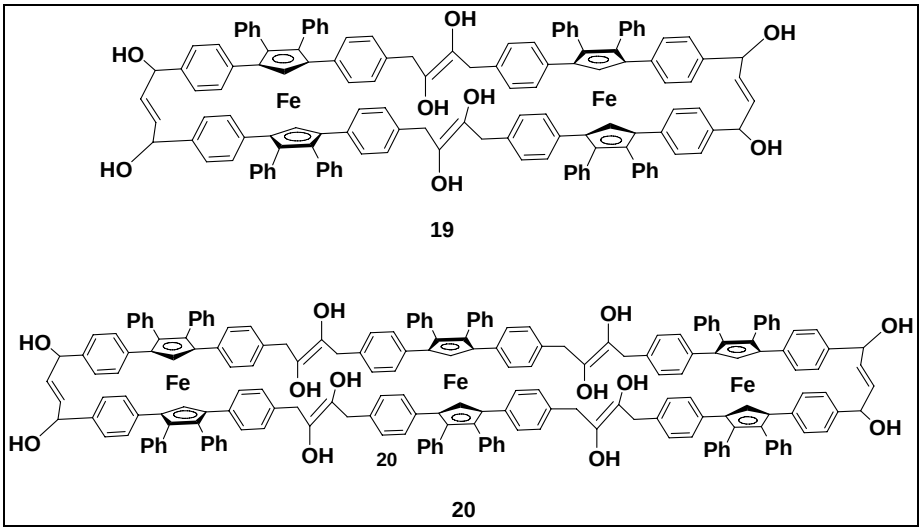


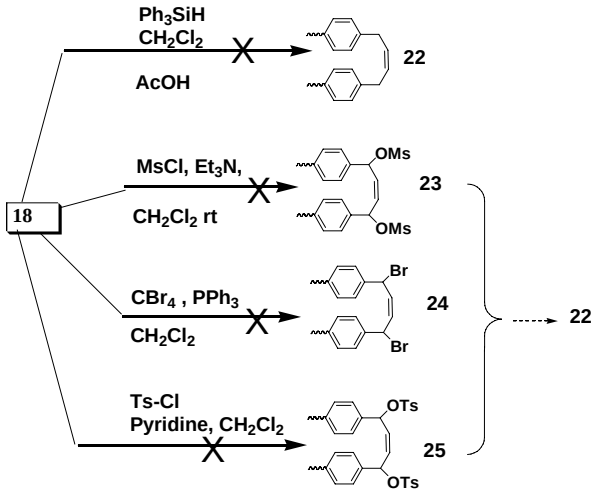
Figure 2.2. Larger Analogues of the macrocyclic ferrocene

Conversion of the completely cyclized higher analogues **(19, 20** etc.) of the macrocyclic ferrocene to higher diameter tubes expands the scope and utility of the protocol to make carbon nanotubes with predetermined diameter and sizes. By this it becomes possible to tailor them for specific application without much of the problems and ambiguities associated with nano tubes materials produced by the conventional methods.[7 - 9] Such methods produced tubes with non-uniform parameters such as size, diameter and type. Such rational approach to carbon nanotubes will enhance and promote their rapid acceleration in commercial applications and in research especially in nano electronic devices where they are greatly sought for consistent and uniform flow of current.[7]

2.3.4: Synthesis of Ferrocenylcyclophane Intermediate 22

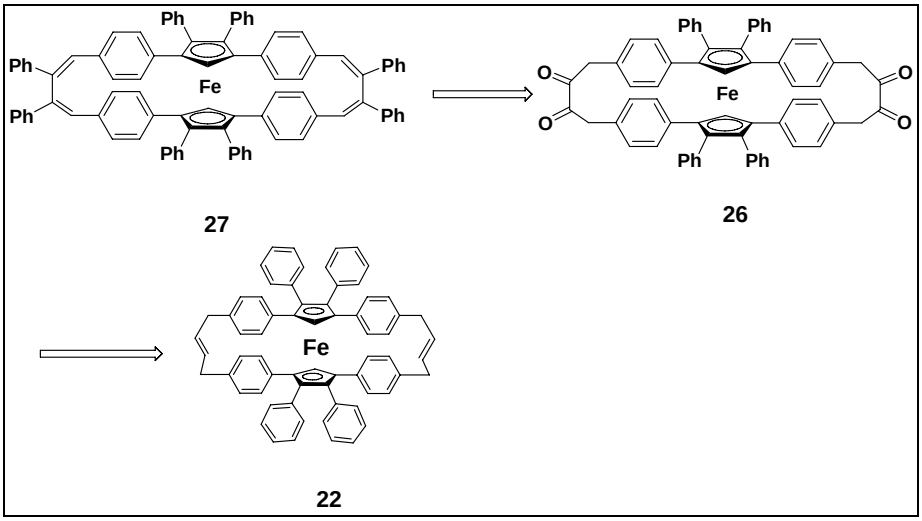
Attempted de-hydroxylation of **18** with triphenylsilane in methylene chloride and acetic acid[50] gave disappointing results with unidentifiable products. After several attempts to remove the hydroxyl functionality failed with this approach, other ways were sought to remove them by converting them to better leaving groups prior to their removal as shown in Scheme 2.10.

Scheme 2.10: Dehydroxylation of tetrahydroxy ferrocenophane 18



This was expected to aid and facilitate the subsequent removal of such groups to the target compound **22**. Groups such as mesylate, bromide, and tosylate were all tried with little to no success as shown in Scheme 2.10. Obtaining **22** was part of a plan to introduce two phenyl groups at positions 1, 1', 2 and 2' through a series of reactions as shown in the retro-synthetic Scheme 2.11.

Scheme 2.11. Retro-synthetic analysis of ferrocenophane 27 from 22

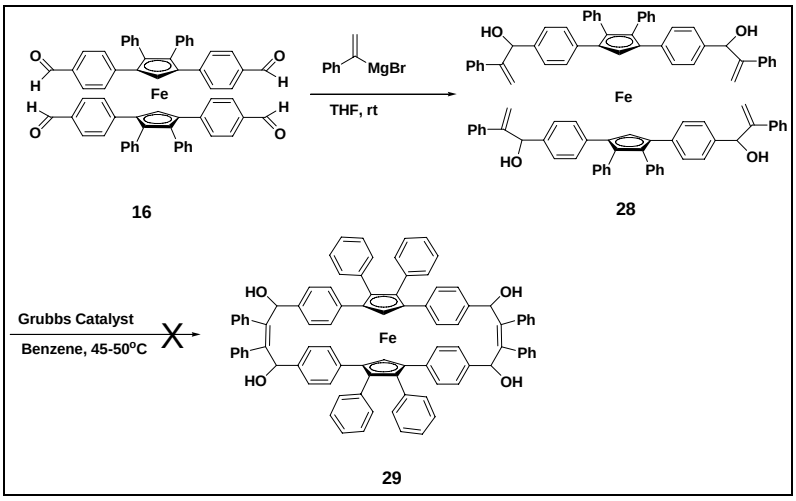


In Scheme 2.11, the tetrahydroxyl compound obtained by treating **22** with osmium tetra oxide (OsO_4) will be oxidized with IBX to convert it to a carbonyl group to obtain the tetracarbonyl compound **26**. This will pave way for the incorporation of the phenyl group by the use of the phenyl lithium in THF. Acidic dehydration of the corresponding adduct will give cyclophane **27**, a critical intermediate.

With such difficulty removing the four hydroxyl groups at the benzyl positions of **18** to get **22**, an alternative scheme was devised where a slight modification was made in the previous Grignard reaction (Scheme 2.8).

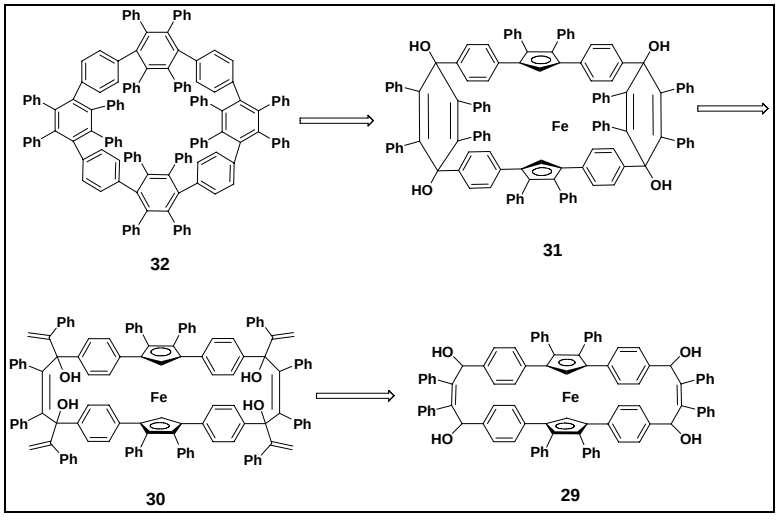
Vinylmagnesium bromide was replaced with styrylmagnesium bromide to afford **28** as shown in Scheme 2.12**.** However, when **28** was subjected to ring closing methathesis using second generation Grubbs catalyst in benzene at 50^{o}C, there was no reaction with 100% recovery of the starting material. Running the reaction at higher temperatures for extended time in excess of 72 hours resulted in the decomposition of the starting material with no evidence of the desired product **29**.

Scheme 2.12. Synthesis of ferrocenophane 29



The successful synthesis of **29** will pave way for the construction of the critical intermediate **32**, a step to the final target **1** as shown in Scheme 2.13. However, several attempts to synthesize **29** were not successful.

Scheme 2.13. Retro-synthetic analysis of macrocyclic beltene 32 from 29

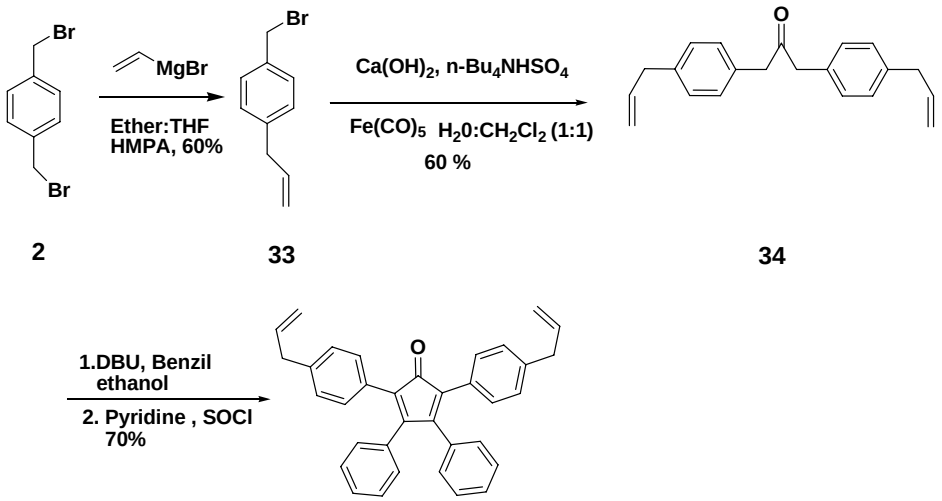


2.3.5. An Alternative route to Ferrocenylcyclophane Intermediate 22

At this point, a new scheme was designed to synthesis intermediate **22** directly without going through the intermediate **18** with hydroxyl groups which had become difficult to remove. This required a slight modification of the original scheme. It was decided to incorporate a vinyl moiety in the early stages of the protocol which will subsequently be used to construct the initial macrocyclic cyclophane by a ring closing alkene metathesis. Such a detour will effectively lead to **22** without going through the tetra-hydroxyl intermediate **18**.

As a result, the dibromide **2** was treated with 1 equivalent of vinlymagnesium bromide in ether/THF (1:1) at room temperature to obtain 1-allyl-4-(bromomethyl)benzene **33** in 60% yield. Carbonylative coupling reaction of the benzyl bromide mediated by iron pentacarbonyl in dichloromethane and water with a phase transfer catalyst at room temperature gave the symmetrical ketone **34**. Aldol-type condensation of **34** with benzil and DBU in ethanol followed by the treatment of the resulting adduct with thionyl chloride in pyridine afforded the cyclopentadienone **35** in 70% yield as shown in Scheme 2.14.

Scheme 2.14. Synthesis of cyclopentadienone 35

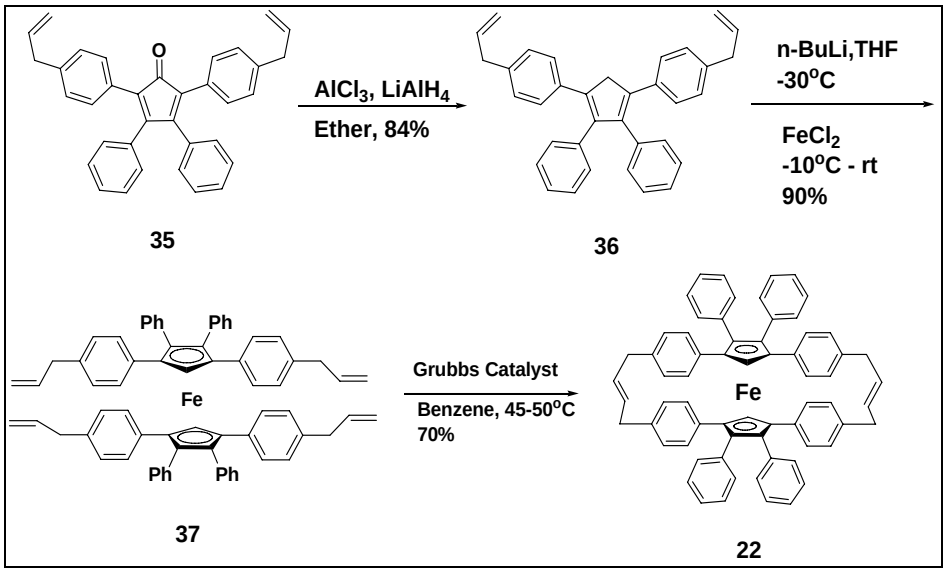


The incorporation of the terminal alkene in **35** will easily allow the construction of the desired macrocyclic ferrocenylcyclophane **22** without the hydroxyl functional groups. Reduction

of **35** with aluminium hydride derived from aluminium trichloride and lithium aluminium hydride in ether gave the cyclopentadiene **36** in 84% yield as shown in Scheme 2.15.

Intermediate **36** was treated with n-BuLi in THF at -78^{o}C .The resulting carbanion was further treated with iron(II) chloride and the reaction allowed to warm slowly to room temperature to give the ferrocenyl intermediate **37** in 90% yield with the prior incorporation of a terminal alkene. The olefin is perfectly positioned for the metathesis reaction to generate the macrocyclic intermediate **22** (Scheme 2.15).

Scheme 2.15. An alternative route to ferrocenophane 22



Treatment of **2.37** with a second generation Grubbs catalyst in benzene at 50^{o}C in high dilution gave the macrocyclic ferrocenylcyclophane **2.22.** This detour allowed the synthesis of the desired critical macrocyclic intermediate without the hydroxyl functional group thus opening the way to perform further chemical elaboration to achieve the target carbon nanotube **1.**

2.4 Future work

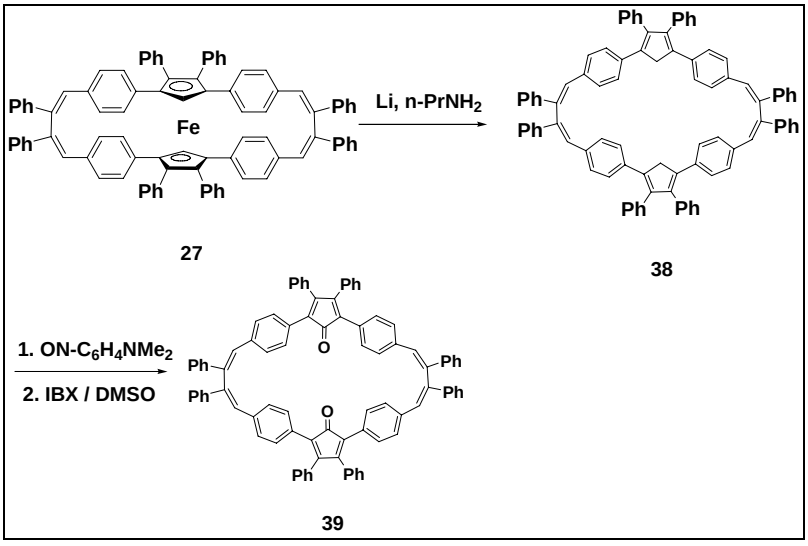
2.4.1: Synthesis of the Macrocyclic Intermediate 2.42

With the synthesis of **22**, the stage has been set for the final chemical elaboration on this macrocyclic ferrocenylcyclophane intermediate to synthesis the target carbon nanotube **1**. There are several possible routes and order of sequences that can be employed to realize the target. Several of the intermediates that has been synthesized and presented above have the potentials to serve as a substrate for the eventual synthesize of the target material through different routes and order of reaction sequence. Such flexibility and versatility makes the success of the developed protocol to synthesize the target carbon nanotube even more promising.

One approach will be to carry out the series of chemical transformations designed to accomplish the task after removing the iron anchor in the ferrocenyl intermediate since it has already served its intended purpose.

However, due to the exceptional stability of the ferrocene, it will be more advantageous to leave it intact at this stage to minimize functional group interference in subsequent reactions and transformations until later stages of the protocol (Scheme 2.11). In the event where difficulties which can be attributed to the presence of the ferrocene are encountered, the iron will be removed before such reactions are performed.

Scheme 2.16: Proposed Synthesis of macrocyclic cyclopentadienone 39



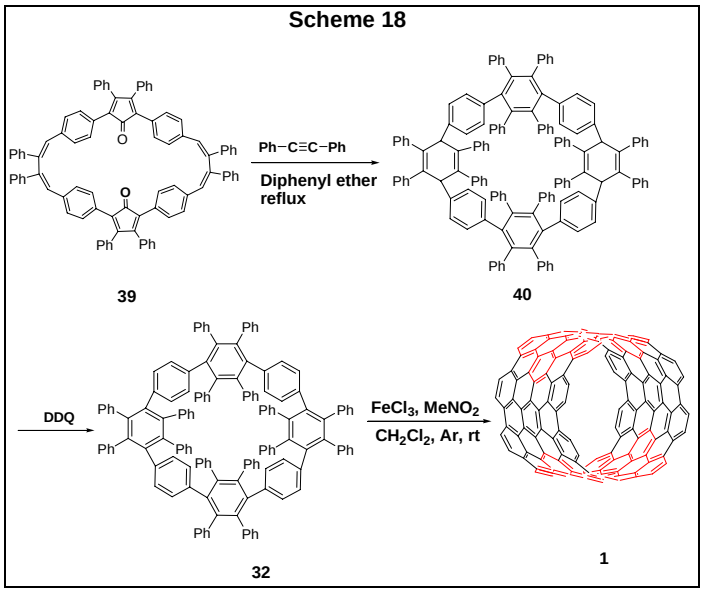
Dihydroxylation of the two double bond linkers in the macrocyclic ferrocenyl intermediate **22** with osmium tetraoxide (OsO_4) and *N*-methylmorpholine-*N*-oxide (NMO) in *t*-butanol / acetone will give the corresponding tetraol. Subjection of this tetraol to IBX oxidation in DMSO is expected to give the tetraketone **26.** Addition of phenyl lithium in THF to **26** followed by acidic dehydration will give the macrocyclic ferrocenyl tetraene **27** (Scheme 2.11).

Addition of phenyl lithium in THF to **26** followed by acidic dehydration will give the macrocyclic ferrocenyl tetraene **27** which will be deironized and oxidized to afford the cyclopentadienone **39** as shown in Scheme 2.16.

2.4.2: Synthesis of the [12, 12] Carbon Nanotube

Quadruple Diels-Alder reaction of **39** with diphenylacetylene in diphenyl ether under reflux (260^{o}C) followed by decarbonylation of the resulting adduct under the prevailing conditions will afford **40.** Subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-quinone (DDQ) will give the completely aromatizes beltene **32**. Oxidative cyclodehydrogenation of **32** with ferric chloride in nitro methane will afford the target unfunctionalized (12, 12) carbon nanotube **1** (Scheme 2.17).

Scheme 2.17: Proposed synthesis of (12, 12) SWNT from 39



2.5: CONCLUSION

After almost a decade after their discovery, carbon nanotubes are yet to be fully integrated into everyday household and commercial products despite their enormous potential applications. The bottleneck in the transition from discovery to application mainly stems from their lack of solubility in most solvents and heterogeneity in terms of length, diameter, and conformation which imparts different electrical and mechanical properties. However, conventional methods of production produce a mixture of all these varieties in addition to large amount of impurities. This requires cumbersome purification and separation procedure under harsh acidic conditions which can be expensive and risky. In addition such treatments may compromise the integrity of the tubes thus limiting their effectiveness in applications.

Functionalization and subsequent solubilization in basic solvents are also limited to few oxidation reactions which usually produce random chemical modifications. The synthesis of (12,12,) arm chair carbon nanotube using a rational synthetic approach via a ferrocene intermediate through a series of carbonylative coupling reaction of benzyl halides and Diels-Alder reaction followed by oxidative dehydrogenation have been presented. This approach has the ability to produce carbon nanotubes with pre-defined length and diameter with the prior incorporation of functional groups leading to their functionalized derivatives for specific desired applications. This procedure can also be expanded to produce carbon nanotubes with heteroatom in their skeleton which are currently not known.

CHAPTER 3 - SYNTHESIS OF CARBON NANOTUBES VIA UN-ASSISITED ALKENE METHATHEIS PATHWAY

3.1: INTRODUCTION AND BACKGROUND

In the previous chapter synthesis of carbon nanotubes via a ferrocenyl intermediate where iron served as an anchor for the efficient cyclization of a critical intermediate to make a macro cyclic ferrocenophane intermediate was proposed.

Alongside the synthesis of the carbon nanotubes via a ferrocenyl intermediate, an un-assisted pathway through ring closing olefin methathesis (RCM) was also being investigated to compare efficiency. This idea was pursued and tested after the removal of the iron from the ferrocene became problematic with our known and tested protocol as described in the preceding chapter.

After the formation of the macrocyclic ferrocenyl intermediate, the iron was expected to be removed to pave way for further chemical elaboration to make the target material **1.** However in the course of that protocol, difficulty in de-ironizing the ferrocenyl intermediate emerged.

This called for further investigation to find an effective way to de-ironized the ferrocene. This de-ironization reaction is currently being investigated. Meanwhile it became interesting to attempt the formation of the critical macro cyclic intermediate without the iron anchor thus by-passing the ferrocenyl intermediate.

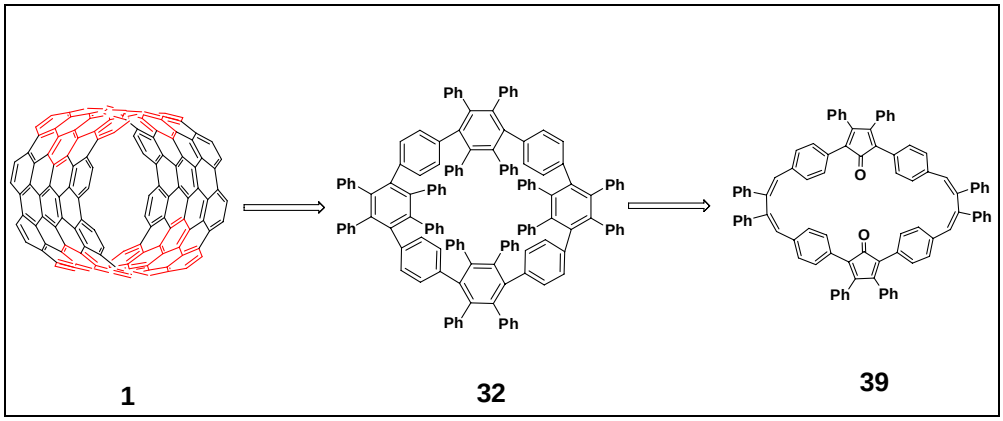
This new approach and detour provided quite and impressive results in terms of yield and purity of the materials. In addition it drastically reduced the synthetic steps that would have been required to make the target material using the original proposed ferrocenyl intermediate as an anchor. By optimizing the reactions, an acceptable balance was found between the yield being realized and the number of steps being reduced by comparing the two approaches.

3.2. Retro-synthetic Analysis

The retro-synthetic analysis of this approach is summarized in Scheme 3.1. Without deviating much from the original plan, it was decided to use one of the initial intermediates

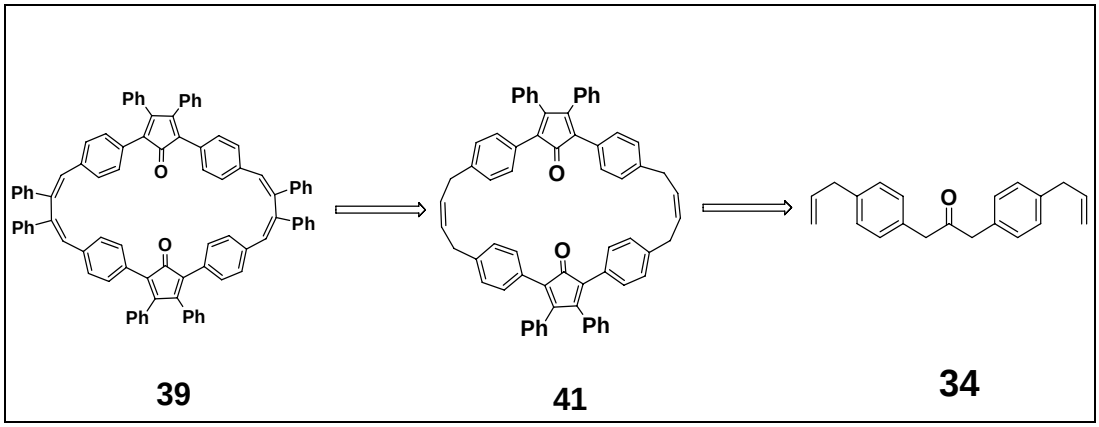
employed in the previous approach (Chapter 2). 1,3-Bis(4-allylphenyl)propan-2-one which has previously been synthesized in the previous chapter was chosen as starting material for this new scheme.

Scheme 3.1. Retro-synthetic analysis of 1 from 39



The construction of intermediate **39** is summarized in the scheme below using 1,3-Bis(4-allylphenyl)propan-2-one (**34**) as the starting point.

Scheme 3.2. Retro-synthetic analysis of macrocyclic cyclopentadienone 39 from 34



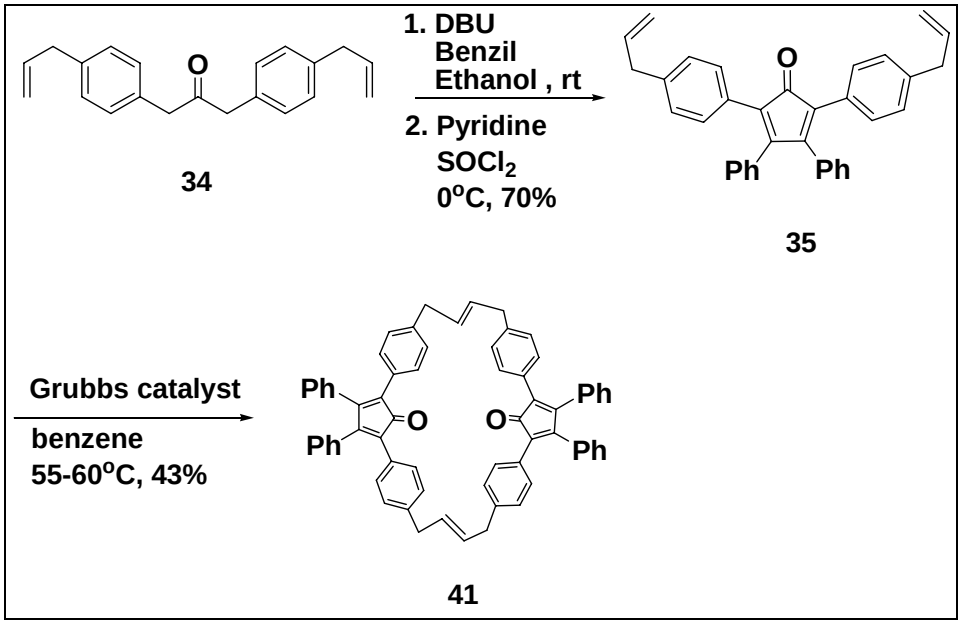
3.3. Synthesis

2.3..: Synthesis of Macrocyclic Cyclopentadienone 41

Aldol addition of 1,3-bis(4-allylphenyl)propan-2-one **(34)** with benzil in ethanol under basic conditions gave the aldol-adduct which was further treated with pyridine in thionyl

chloride to give the cyclopentadienone **35** in 70% yield.[48] This was directly subjected to a ring closing methathesis using a second generation Grubbs catalyst in benzene. This reaction was performed under high dilution to reduce and to prevent polymerization of the starting material. This afforded the critical macro cyclic intermediate **41** in 43% yield as shown in Scheme 3.3.

Scheme 3.3. Synthesis of macrocyclic cyclopentadienone 41 via ring-closing methathesis without a ferrocene anchor



However there was significant isomerization of the starting material with at least a shift in one of the terminal double bonds to an internal double bond. Incomplete cyclization products with similarly shifted terminal double bonds to internal ones were also observed as shown in Figure 3.1.

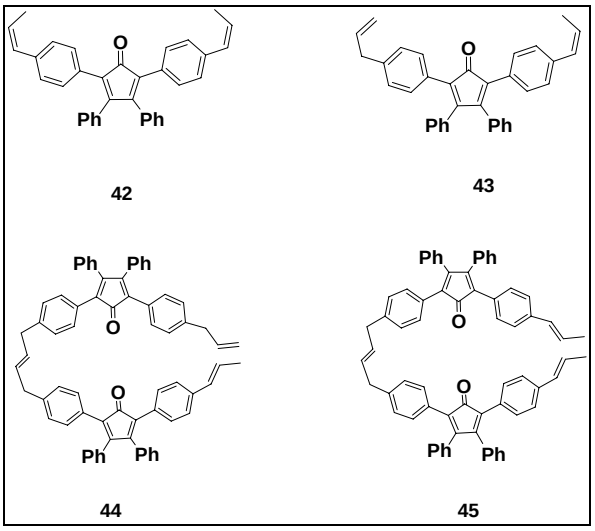
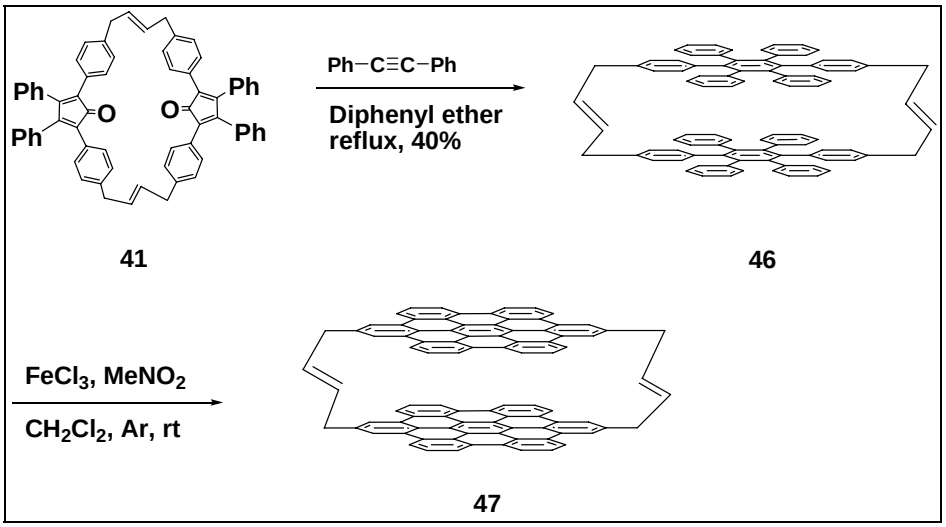


Figure 3.1. Some isomerized incomplete cyclized by-products of the RCM

3.3.2. Synthesis of Hexa-peri-benzocoronene Cyclophane (HBCC) –A macrocyclic "Superbenzene" (47)

At this point it was decided to test the efficiency of the proposed Diels-Alder reaction which is central to the success of this project. The macrocyclic cyclopentadienone intermediate **41** was made to react with diphenyl acetylene in diphenyl ether under reflux.[47,51,52] This afforded the perfectly symmetrical fully substituted triphenylophane intermediate **46** in 40% yield after decarbonylation of the Diels-Alder adduct under the prevailing conditions. The figure below shows the crystal structure of **46** crystallized from methylene chloride by slow evaporation of solvent.

Scheme 3.4. Synthesis of 2, 36-Diene[4.4]hexa-peri-hexabenzocoronenophane (HBCC) 47



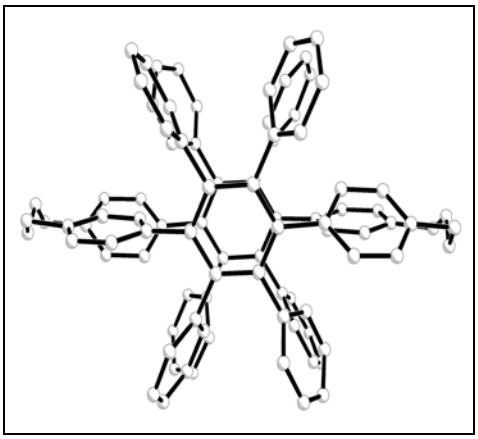
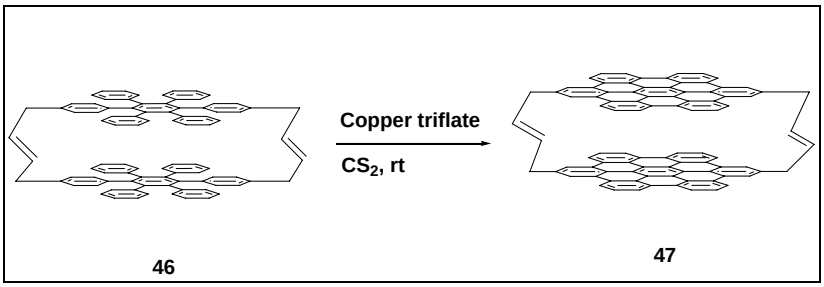


Figure 3.2. Single-crystal X-ray analysis of the triphenylophane 46

Lewis acid mediated oxidative dehydrogenation of the substituted phenyl rings around the central benzene using iron(III) chloride in methylene chloride will cyclize **46** to give two hexa-*peri*-hexabenzocoronenyl (HBC) moieties connected by an unsaturated aliphatic linker – a macrocyclic "superbiphenyl" **47**.[51, 53] Such coronene compounds and their alkyl substituted derivatives exhibit discotic mesophases over a large range of temperatures. They are known to act as photoconductors exhibiting high charge carrier mobility with useful application in electric solar panels.[52, 54, 55] This cyclization is very critical will be used in realizing the final target **1.**

Alternatively, **46** may also be dehydrogenated by a cylization procedure utilizing a mixture of copper(II)-trifluromethanesulfonate and $AlCl_3$ in carbon disulfide at room temperature[51] as shown in Scheme 3.5.

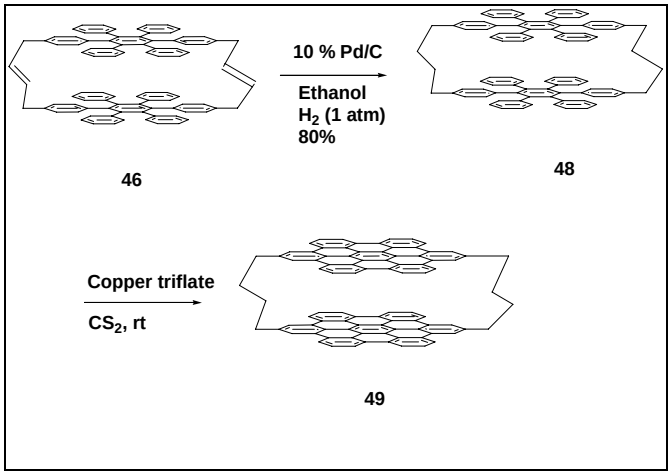
Scheme 3.5. An alternative route to HBCC 47



The enormous potential applications of many of such planarized HBCs and their larger analogues in electrochemistry, fabrication of solar and nano electronic devices suggest their macrocyclic analogues could be useful as well and hopefully with better and more profound electronic properties.[57]

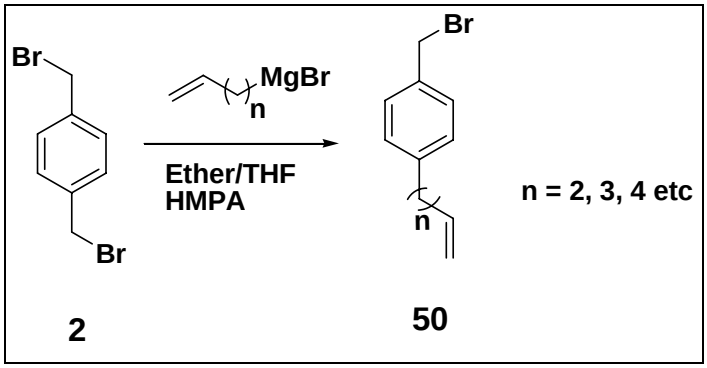
It was therefore envisaged that testing the properties of such a macrocyclic "superbenzene" could even have greater potentials than the one dimensional planar HBC and their substituted derivatives.[51, 52, 57]

Scheme 3.6. Synthesis of HBCC 49 with a saturated alkyl linker

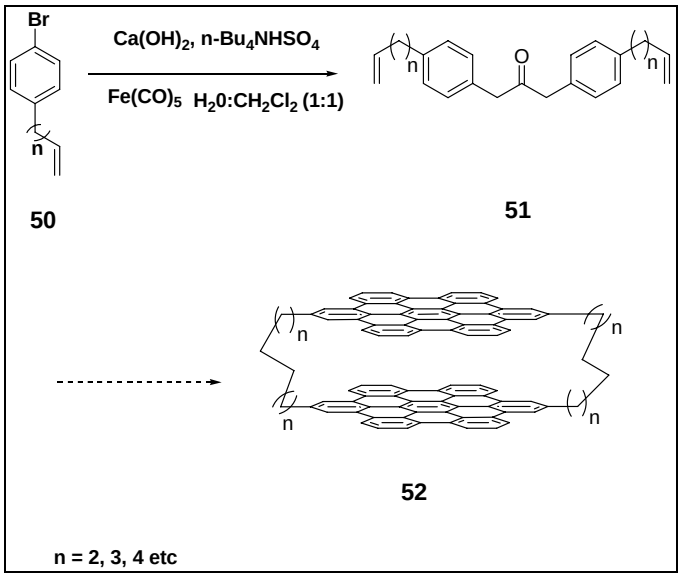


The unsaturated alkene linker in **46** was reduced with 10% Palladium on carbon (Pd/C) under 1 atm of hydrogen gas to obtain **48** in 80% yield. Cyclization by oxidative dehydrogenation of **48** using mixture of copper(II)-trifluromethanesulfonate and $AlCl_3$ in carbon disulfide at room temperature[51] will give the macrocyclic HBC **49** with a butyl chain linker.

Scheme 3.7. Proposed synthesis of bromomethyl benzene with extended terminal alkene



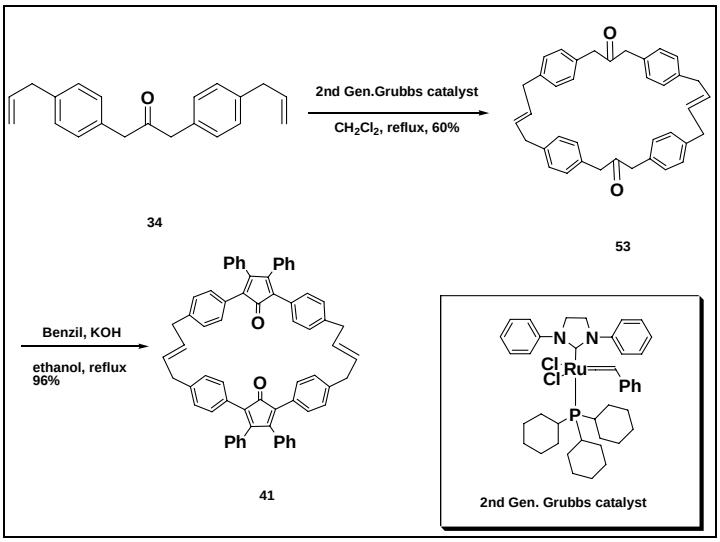
Scheme 3.8. Proposed Synthesis of HBCC 52 with extended alkyl chain linker



This alkyl chain linker can be lengthened by modifying the scheme as described above to make different HBCC for future testing and to explore their electronic properties (Scheme 3.7 and 3.8).

To optimize the protocol and to minimize the isomerization of the terminal alkene during the construction of **41** (Scheme 3.3), the reaction sequence was revised. As a result, the ring closing metathesis was performed with the starting material **34** before further chemical elaboration towards the final target was attempted as shown in Scheme 3.9.

Scheme 3.9. An alternative route to cyclopentadienone 41



Treatment of **34** with a second generation Grubbs catalyst in methylene chloride under reflux gave the macrocyclic diketone **53** in 60% yield after silica gel column chromatography. The structure of **53** was unequivocally determined by a single-crystal analysis.

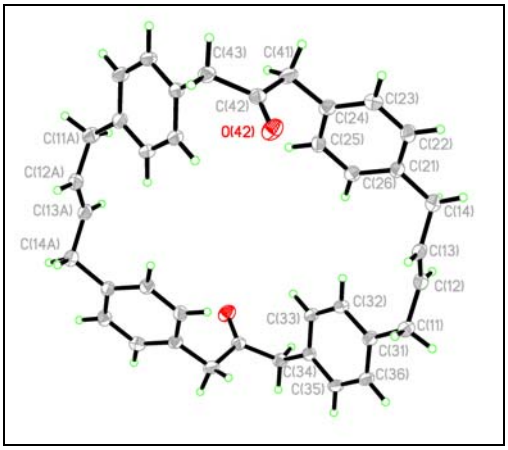


Figure 3.3. Single-crystal X-ray analysis of the paracyclophane 53

Subjection of **53** to an aldol-like type condensation with benzil in ethanol with potassium hydroxide under reflux gave the cyclopentadienone **41** in 96% yield as shown in Scheme 3.9.

Such an approach also reduced the bulkiness of the starting material for the alkene metathesis step thus significantly reducing reaction time from 72 hours to 18- 24 hours. In addition there were fewer amounts of the incomplete cyclization and isomerized side products shown in Figure 3.1.

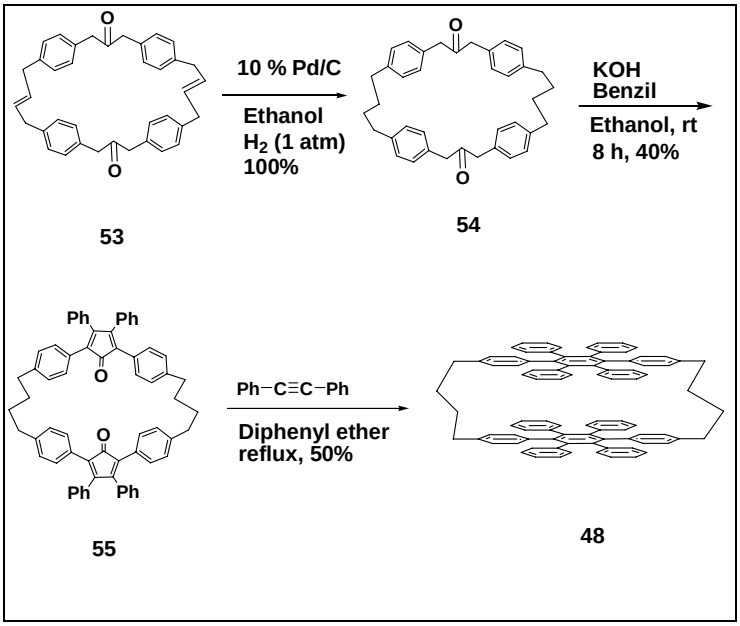
In this scheme it was also realized that, methylene chloride, a significantly less toxic solvent than benzene could be used as the solvent since the reaction could be performed at a much lower temperature due to the absence of the phenyl groups at this stage. Overall, this detour led to improved yield and efficiency in the synthetic effort.

The presence of the double bond linker in **41** was suspected to be the reason for the seemingly low yield of the Diels-Alder reaction (Scheme 3.4). The high temperature of refluxing diphenyl ether at over 260^{o}C seems to present a very harsh condition for the unsaturated double bond linker. Large amounts of yellowish solid material were obtained. NMR analysis of this by-product was not sufficient to effectively characterize it. Literature search revealed in all the cases that such conditions have been used to effect this reaction, there were no other functionality

present except saturated alkyl substituents and in such cases higher yields were reported. Also it was envisaged that replacing the alkene linker in **53** with a saturated alkyl linker would possibly lengthen the linker and allow the aldol addition to proceed more smoothly and effectively.

In view of the above analysis, the diketone **53** was treated with 10% palladium on carbon in ethanol under 1 atmosphere of hydrogen gas. This led to the hydrogenation of the double bond to afford **54** in quantitative yield as shown in Scheme 3.10.

Scheme 3.10. An alternative synthetic route to triphenylophane 48



Condensation of **54** with benzil and potassium hydroxide in ethanol followed by treatment with thionyl chloride in pyridine gave the macrocyclic cyclopentadienone **55** having n-butyl chain linker in 40% yield**.**

A double Diels-alder reaction of **55** with diphenylacetylene in diphenyl ether at 260^{o}C gave the cyclophane **48** in 50% yield as shown in Scheme 3.9. Cyclization of **48** by oxidative dehydrogenation using a mixture of copper(II)-trifluromethanesulfonate and $AlCl_3$ in carbon disulfide at room temperature[51] will give hexa-peri-hexabenzocoronenophane **49** with a butyl chain linker (Scheme 3.6).

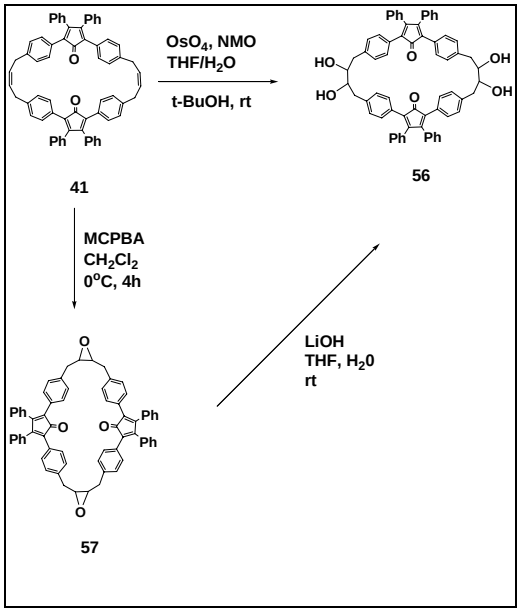
3.4 Future work

3.4.1. Proposed Synthesis of [12, 12] Arm Chair Carbon Nanotube

Having synthesized the critical macrocyclic cyclopentadienone **41** without going through the ferrocenyl intermediate, the overall steps in the project have been extensively reduced. This will ultimately improve efficiency and the overall yield. This will allow the production of carbon nanotubes with predefined length and diameter with possible functionalization tailored for specific applications to be produced in kilogram scale for the first time since its discovery in 1991. The unsaturated alkene linker is crucial since it will serve as a point for the introduction of other desired moieties needed for the eventual realization of the target carbon nanotube **1.**

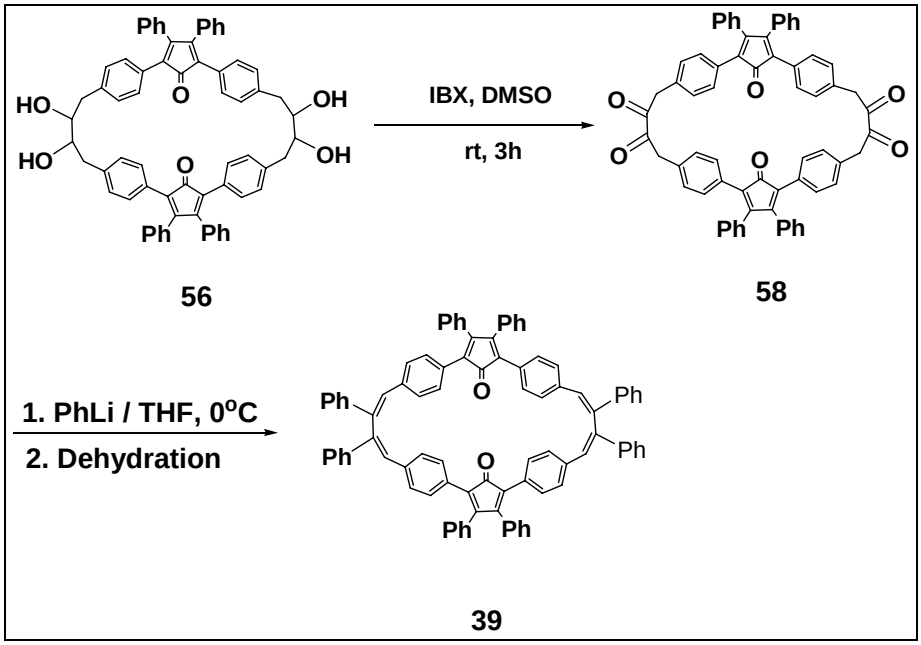
Dihydroxylation of the alkene linker in **41** with osmium tetraoxide and NMO in THF / water / t-butanol will give tetraol **56.** Alternatively treating **41** with MCPBA in methylene chloride at 0^{o}C for 4 hours affords the corresponding epoxide **57.** Opening of the epoxide ring under basic conditions with Lithium hydroxide (LiOH) in THF and water at room temperature will afford **56** as illustrated in Scheme 3.11.

Scheme 3.11. Dihydroxylation of double bond in cyclopentadienone 41



Treatment of the tetraol **56** with IBX in DMSO will produce compound **58** which will be converted to the tetraene **39** after treating with phenyl lithium in THF at 0°C followed by acidic dehydration as shown in scheme 3.12.

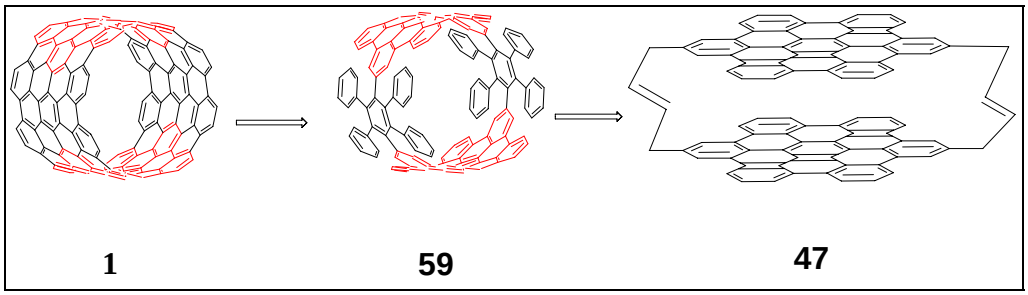
Scheme 3.12. Proposed synthesis of intermediate 39



Quadruple Diels-Alder reactions of **39** with diphenylacetylene in diphenyl ether under reflux (260°C) followed by decarbonylation of the resulting adduct will afford **40**. Subsequent oxidation of **40** with DDQ will furnish the completely aromatized beltene **32**. Oxidative dehydrogenation of **32** with ferric chloride in nitromethane will give the target unfunctionalized (12, 12) arm chair carbon nanotube target **1** (Scheme 2.18).

The versatility of the protocol and the proposed methodology presented in this dissertation allows several routes and detours to be taken to achieve the synthesis of the intended target and its derivatives. For example, intermediates **47** and **53** could be taken on different routes other than the ones presented above to achieve the same goal of synthesizing **1** and its derivatives. An alternative route (Scheme 3.13) depicted by the retro-synthetic analysis below will be pursued especially in the event of unforeseen difficulties in efficiently and effectively accomplishing any of the above synthetic chemical conversions towards the target material.

Scheme 3.13. Retro-synthetic analysis of SWNT from coronenophane 47

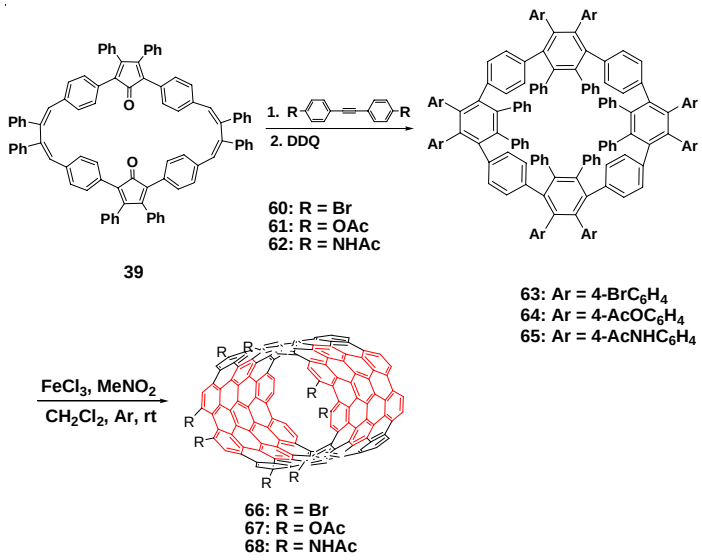


Also the macrocyclic intermediate **53** (scheme 9) can be used in a series of chemical conversions and manipulations to make the intended target. This will require a slightly different set of reactions and or order of reaction sequences from the schemes presented above. This observation greatly underscores the importance and versatility of the protocol and methodology presented in this dissertation.

3.4.2. Synthesis of Functionalized Carbon Nanotubes

Chemical manipulation or functionalization and subsequent solubilization of carbon nanotubes in basic organic solvents are crucial if it is to be effectively applied in most of its potential applications. However, none of the currents methods of production has the ability to incorporate any functionality into the tubes in the course of their production.

Scheme 3.14. Proposed synthesis of various functionalized SWNTs from intermediate 39

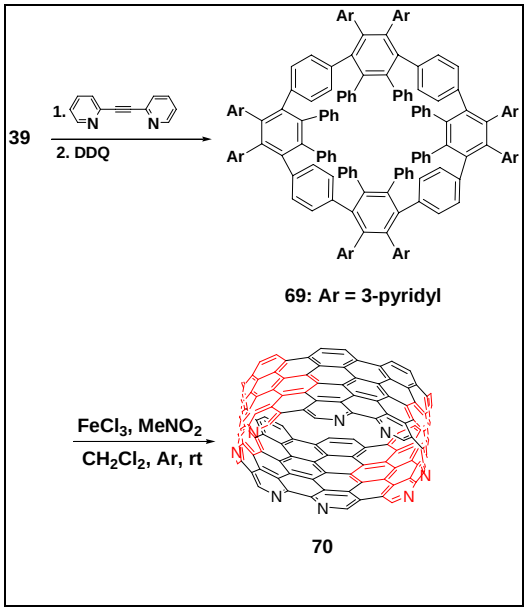


Although several methods are available to functionalize carbon nanotubes, such procedures usually results in randomized reactions and the degree of functionalization is also uncertain. Plasma oxidation of tube tips after side wall protection with polystyrene matrix resulted in the incorporation of carboxylic acid functionality whilst preserving the integrity of the side wall. However, the level of substitution and location of the carboxyl groups are difficult to determine.

The protocol discussed and presented in this dissertation lends itself for expansion to produce such functionalized carbon nanotubes with predetermined size and length. Functionalities or groups such as F, Cl, Br, OR, OAc, OH, COOH, CO2R will be incorporated in the tubes by employing starting materials which has been prior substituted with such groups (Scheme 3.14). Other functional groups that can be used include NR_2, NHAc, NHCOR, $NHSO_2R$, SH, SR, PR_2 or $PO(OR)_2$, where R can be hydrogen, phenyl or and alkyl chain.

A synthetic procedure detailing how to make carbon nanotubes functionalized at the tips with various functional groups is presented in Scheme 3.14. In most cases the attached functional groups may potentially be employed to link biologically active chemicals as a means of drug delivery vehicles to targeted organs.

Scheme 3.15. Proposed Synthesis of heteroatom containing nanotube



Also these methods as discussed in this dissertation will be applied to the production of nanotubes containing heteroatom by prior incorporation of such atoms in the starting materials. Quadruple Diels-Alder of **39** with dipyridylacetylene and subsequent aromatization with DDQ will afford **69**. Subjecting **69** to an oxidative dehydrogenation reaction with $FeCl_3$ in nitromethane and methylene chloride will give a heteroatom-containing (12, 12) nanotube (**70**) with eight nitrogen atoms at the tip as shown in Scheme 3.15.

3.5. CONCLUSION

A rational, stepwise synthetic approach to (12, 12) SWNT and its functionalized derivative with pre-defined length and diameter have been investigated and presented. This on-going project has led to hexa-peri-hexabenzocoronenophane which is known to have exceptional electronic properties and has enormous application in the fabrication of materials for solar energy panels. The expansion of the procedure to produce carbon nanotubes with heteroatom incorporated into their skeleton backbone has also been proposed and is currently under investigation in Hua's Lab.

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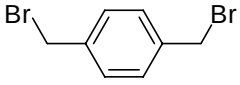
CHAPTER 4 - EXPERIMENTAL SECTION

General Methods. Unless other wise stated, Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian 400 MHz and Varian 200 MHz instrument, for proton NMR; Varian 100 MHz and Varian 50 MHz instrument, for carbon NMR. The NMR spectra were obtained in chloroform-*d* ($CDCl_3$) unless otherwise stated. The chemical shifts are given in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard, unless other wise stated. Coupling constants (J) are given in hertz. Solvents were dried by distillation under argon from CaH_2 (CH_2Cl_2, pyridine, Et_3N, DMF, diisopropylamine), Na-Ph_2CO (THF, Et_2O), Mg (EtOH, MeOH), and LAH (toluene, benzene). $FeCl_2$ was purchased from Strem Chemical Company. All other reagents were obtained from either Aldrich Chemical Company or Fisher Chemical Company and were used without further purification. All reactions were performed under argon atmosphere, unless otherwise stated. Thin layer chromatography (TLC) was performed on plates obtained from Aldrich and flash column chromatography was performed on silica gel (200-400 mesh) from Natland Corporation. Mass spectra were obtained from a Brucker Esquire 3000 Plus electrospray ionization mass spectrometer and a MALDI-TOF/TOF MS instrument, Model; Ultraflex II (Brucker Daltonics). High Resolution mass spectra were taken with an IonSpec HiResMALDI mass spectrometer using 2, 5-dihydroxybenzoic acid as a matrix.

Experimental Methods for Chapter 2

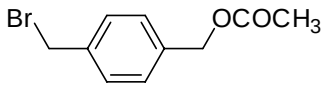
Synthesis of 1,4-Bis(bromomethyl)benzene (2)



(SR-01-24)To a solution of p-xylene (45 ml, 0.365mol) in 600 ml of benzene were added 129 g of NBS (0.731 mol) and 3.38 g of benzoylperoxide (0.015 mol). The mixture was refluxed for 4 hours. Half of the benzene was evaporated off and the mixture gradually cooled to 0^oC to obtain

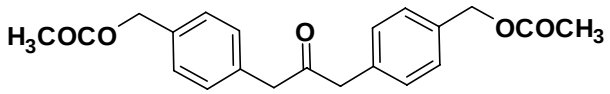
a white precipitate. This was vacuum-dried overnight to obtain 58.0g (60 % yield) of **2** as white solid.[1]H NMR (CDCl3) δ 7.37 (s, Ar-H); 4.48 (s, 4 H, Ar-CH_2-Br), [13]C NMR (CDCl3) δ 138.22, 129.70, 33.02

Synthesis of 4-(Bromomethy)benzyl acetate (3)



(Bw-4-104) A mixture of **2** (13.37g, 50.64 mmoles) and 4.96 g of potassium acetate (4.96 g, 50.54 mmol) was vacumm-flame dried thoroughly and purged with argon. To this was added 100 ml of acetonitrile and the mixture allowed to stir at room temperature overnight (12 hours). The solvent was then evaporated away and the residue was dissolved in ethyl acetate, quenched with aqueous ammonium chloride. The organic layer was washed with brine and concentrated to dryness. The crude product was subjected to silica gel column chromatography using a mixture of petroleum ether and ethyl acetate to obtain 7.15 g (65.5% yield) of **3** after 1.5 g (11%) of recovered starting material. [1]H NMR (CDCl3) δ7.39 (d, J = 8 Hz, 2H, Ar-H),7.34 (d, J = 8Hz, 2H, Ar-H), 5.10 (s, 2H, CH_2OAc), 4.49 (s, 2H, CH_2Br), 2.11(s, 3H, -CH_3); [13]C NMR 170.99, 137.95, 136.35, 129.43, 128.82, 128.49, 126.91, 65.93, 33.19, 21.18.

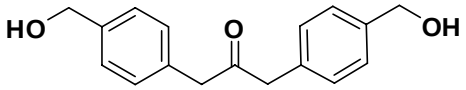
Synthesis of (4, 4'-(2-Oxopropane-1,3-diyl)bis(4,1-phenylene))bis(methylene) diacetate (4)



(Bw-5-25, Bw-8-11) Tetrabutylammonium hydrogensulfate (0.80 g, 2.37 mmol) and calcium hydroxide (1.40 g, 18.90 mmol) were weighed into a two-necked flask, vacuumed-flame dried and dissolved in 100 ml of de-gassed methylene chloride/water mixture (1:1) under argon. To this was added 2.30 g (9.47 mmol) of **3** followed by 0.62 ml (4.73 mmoles) of iron pentacarbonyl. The mixture was stirred for 5 hours at 20°C. Air was bubbled through the mixture to destroy excess iron pentacarbonyl. The mixture was diluted with ethyl acetate and filtered through a sintered glass to remove the solid brown precipitate. The filtrate was diluted with

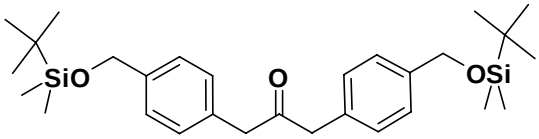
aqueous ammonium chloride and the organic layer extracted (3 times) with ethyl acetate, washed with brine and concentrated to dryness. The crude product was subjected to silica-gel column chromatography employing hexane / ethyl acetate (2:1) mixture as eluant to obtain 1.27 g (76% yield) of **4**. ^{1}H NMR ($CDCl_3$) δ 7.32 (d, J = 8 Hz, 4H, Ar), 7.16 (d, J = 8 Hz, 4H, Ar), 5.09 (s, 4H, CH_2OAc), 3.73 (s, 4H, CH_2CO), 2.11 (s, 6H, CH3); ^{13}C NMR 207.2, 171.5, 135.0, 134.1, 129.9, 128.9, 66.1, 49.0, 21.2

Sunthesis of 1,3-Bis(4-(hydroxymethyl)phenyl)propane-2-one (6)



(Bw-4-107) A solution of **4** (0.79 g, 2.22 mmoles) and potassium carbonate (1.22 g, 8.87 mmoles) in methanol was stirred at room temperature under argon for 5 hours. The methanol solvent was removed under vacuum and the residue diluted with ethyl acetate. The solution was quenched with 1M aqueous hydrochloric acid. The organic layer was extracted 3 times with ethyl acetate and washed with brine, dried over anhydrous sodium sulfate and concentrated to dryness to obtain **6** (0.54 g, 91 % crude yield). The crude material was used in the next step without further purification. ^{1}H NMR (CDCl3) δ 7.32 (s, J = 8 Hz, 4H, Ar), 7.15 (d, J = 8 Hz, 4H, Ar,), 4.69 (s, 4H, CH_2OH), 3.73 (s, 4H, CH_2CO), 1.59 (bs, 2H, OH); ^{13}C NMR 206.2 (s, CO), 139.9, 133.3, 129.8, 127.6, 64.9, 49.0

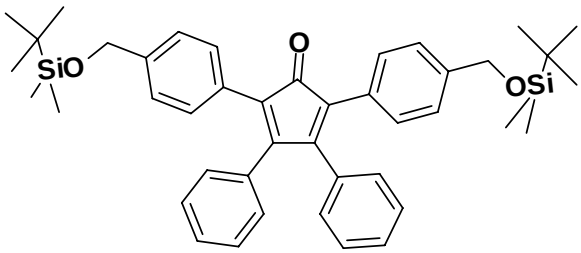
Synthesis of 1,3-Bis(4-((tert-butyldimethylsilyloxy)methyl)phenyl)propane-2-one (7)



(Bw-5-99, Bw-8-16) A mixture of **2.6** (0.54 g, 2.00 mmoles) and DMAP were weighed into a flask and dried thoroughly. Dry distilled methylene chloride and triethylamine were added to the mixture and stirred for 30 minutes at room temperature. *Tert*-butyldimethylsilyl chloride (TBDMS-Cl) (1.21 g, 8.05 mmol) was then added and the reaction made to stir at room temperature for 20 hours to completion. The mixture was diluted with diethyl ether and

quenched with aqueous ammonium chloride. The organic layer extracted, washed with brine, dried over anhydrous sodium sulfate and concentrated to dryness. The crude material was subjected to silica-gel column chromatography to obtain 1.0 g (100 %) of **7**. ^{1}H NMR (CDCl3) δ 7.27 (d, J = 8 Hz, 4H, Ar), 7.11 (d, J = 8 Hz, 4H, Ar), 4.73 (s, 4H, CH_2OSi), 3.69 (s, 4H, CH_2CO), 0.94 (s, 18H, t-Bu), 0.10 (s, 12H, MeSi); ^{13}C NMR 206.0, 140.5, 132.8, 129.5, 126.6, 64.9, 48.9, 26.2, 18.6, -5.1.

Synthesis of 2,5-Bis(4-((tert-butyldimethylsilyloxy)methyl)pheny)-3,4-diphenylcyclopenta-2,4-dienone (9)

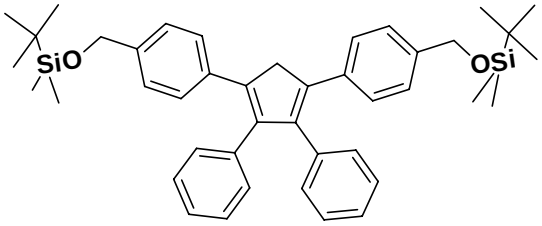


(Bw-5-52, Bw-5-102) An ethanol solution of compound **7** (2.18 g, 4.377 mmol) in a round bottom flask was purged with argon and DBU (0.67 ml, 4.377 mmoles) was added. The mixture was made to stir at room temperature for 30 minutes. An ethanol solution of benzil (0.92 g, 4.377 mmoles) was added by canular .The resulting mixture was allowed to stir at room temperature overnight (~ 18 hours). Solvent was evaporated off and the resulting residue was dissolved in ethylacetate. The solution was then quenched with saturated ammonium chloride solution and the organic layer extracted, dried over anhydrous sodium sulfate and concentrated to dryness.

The crude material was treated with 10.0 ml of pyridine and 2.0 ml of thionyl chloride ($SOCl_2$) at 0^{o}C for 20 minutes. The reaction mixture was diluted with diethyl ether and the solution quenched with saturated aqueous ammonium chloride. The organic layer was extracted, washed with brine and dried over anhydrous sodium sulfate. The dry solution was concentrated to dryness and subjected to silica gel column chromatography to give 2.50 g of compound **9** in 86.0% yield as dark purple solid . Gradient of hexane / diethyl ether mixture was used as eluant. ^{1}H NMR ($CDCl_3$) δ 7.25 – 7.14 (m, 14 H, Ar-H), 6.92 (d, J = 7, 4 H, Ar-H), 4.71 (s, 4 H,

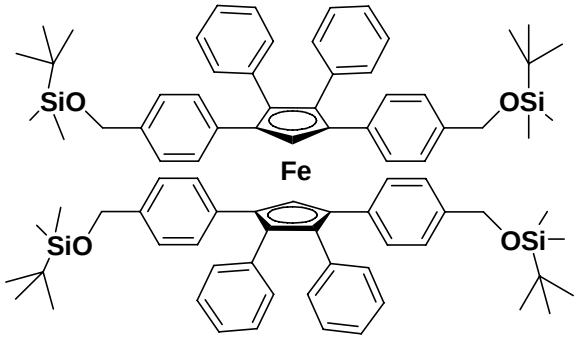
CH_2OSi), 0.93 (s, 18H), 0.08(s,12H); ^{13}C NMR δ 208.0, 154.4, 140.8, 135.1, 133.4, 130.2, 130.1, 129.6, 129.2, 128.6, 128.2, 125.9, 125.4, 65.0, 26.2, 18.6, -5.0

Synthesis of (4,4'-(4,5-Diphenylcyclopenta-3,5-dien-1,3-diyl)bis(4,1phenylene))bis(methylene)bis (oxy)bis(tert-butyldimethylsilane) (10)



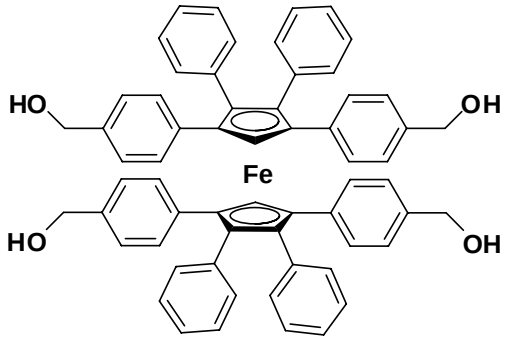
(Bw-5-60, Bw-5-105) An ethereal solution of **29** (0.150 g, 0.223 mmoles) in a two-necked round bottom flask was added $AlCl_3$ (0.15 g, 1.12 mmol) and $LiAlH_4$ (0.004 g, 0.105 mmol) (LAH) at 0^oC. The purple color was immediately discharged to give a yellowish-green solution which was put to reflux at 35oC for 5 hours. The mixture was quenched with iced cold water and the organic layer extracted with diethyl ether. The organic layer was washed with water, brine and dried over anhydrous sodium sulfate. The ethereal solution was concentrated to dryness and subjected to silica-gel column chromatography using hexane and diethyl ether mixture as eluant to obtain 0.088 g of compound **10** (60.0% yield). ^1H NMR (CDCl3) δ 7.15 (m, 14H), 6.97 (m, 4H), 4.68 (s, 4H, CH_2O), 4.01 (s, 2H, CH_2), 0.92 (s, 18H), 0.08 (12H); ^{13}C NMR δ 144.3, 139.5, 136.7 135.2, 129.9, 128.3, 127.7, 126.6, 126.0, 125.9, 64.8, 45.9, 26.0, -5.24

Synthesis of 1,4,1',4'-Tetra[4-(t-butyldimethylsilyoxy)methylphenyl]-2,3,2',3'-tetraphenylferrocene (11)



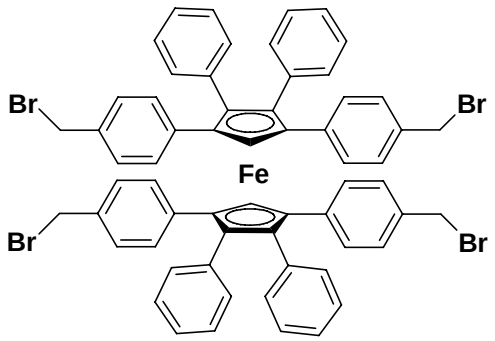
(Bw-5-107, Bw-5-111) Intermediate **10** (0.303 g,0.45mmoles) was weighed into a two-necked round bottom flask along with a stir bar with an attached glass delivery tube. Iron(II) chloride (0.058 g, 0.460 mmol) was weighed into a small round bottom flask in a glove box and attached to the delivery tube. The above setup was thoroughly vacuum-flamed dried and purged with argon. Dry THF (5 ml) was added to dissolve **10** followed by addition of 0.58 ml of 1.2 M *n*-butyl lithium at -78^{o}C. The resulting dark blue solution was stirred for one hour. The iron (II) chloride was transferred into the solution through the delivery tube and the reaction made to warm to room temperature for 15 hours. The mixture was diluted with ethyl acetate and with aqueous ammonium chloride. The organic layer was extracted, washed with brine, dried over anhydrous sodium sulfate and concentrated to dryness. The crude product was subjected to silica-gel column chromatography to obtain compound **11** (0.22 g, 70% yield) as red solid after recovery of some starting material. MS (electrospray ionization) m/z 1370.60 (M^+, 100%), 1371.40 (M+1); exact mass Calcd for $C_{86}H_{106}FeO_4Si_4$: 1370.65 (M^+); ^{1}H NMR (CDCl3) δ 7.05 (d, J = 8 Hz, 8H), 6.96 – 6.90 (m, 20H), 6.83 (t, J = 8Hz, 8H), 5.49 (s, 2H, Cp), 4.62 (s, 8H, CH_2O), 0.94 (s, 36H), 0.09 (s, 24 H); 13C NMR 139.4, 135.2, 134.1, 132.3, 129.2, 126.8, 126.1, 125.4, 91.4 (Cp), 86.0 (Cp), 67.8 (Cp), 65.0 (CH_2O), 26.0, -5.2

Synthesis of 1,4,1',4'-Tetra[4-(hydroxymethyl)phenyl]-2,3,2',3'-tetraphenylferrocene (12)



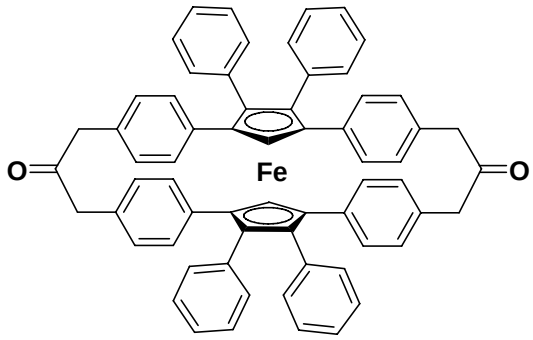
Dry THF solution of 0.300 g of compound **11** (0.219 mmol) was treated with 0.44 ml of 1 M *tert*-butyl ammonium fluoride solution in THF under argon. The mixture was made to stir at room temperature for 4 hours. The reaction was quenched with water and extracted with ethyl acetate several times. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate and concentrated to dryness. The crude product was subjected to silica-gel column chromatography using hexane/ethylacetate mixture as eluant to obtain 0.200 g of compound **12** (100% yield). MS (HiRes MALDI) m/z 914.2417; Calcd for $C_{62}H_{50}FeO_4$: 914.3059 (exact mass); ^{1}H NMR (CDCl3) δ 7.30 – 6.70 (m, 36H, Ar-H), 5.46 (s, 2H, Cp), 4.70 – 4.5 (m, 8H, CH_2O); ^{13}C NMR (D_2O – CH_3OD) 139.9, 136.0, 132.3, 129.4, 127.1, 126.7, 126.5, 118.8, 90.9 (Cp), 80.9 (Cp), 64.4 (CH_2O).

Synthesis of 1,4,1',4'-Tetra[4-(bromomethyl)phenyl]-2,3,2',3'-tetraphenylferrocene (13)



In a two-necked flask was added NBS (0.106g, 0.610 mmol) along with a stir bar. The flask was vacuumed-flame dried and maintain under argon. To this was added 5ml of methylene chloride and 55µl of dimethyl sulfide at 0^oC. A yellow precipitate of sulfonium salt was immediately formed and the mixture was stirred for 15 minutes and cooled to -20^oC. A solution of the tetraol **(12)** (0.093 mg, 0.1016 mmoles) in methylene chloride was added to the preformed sulfonium salt. The yellow solids dissolved immediately to give a solution of red coloration which was stirred at 0^oC for 3 hours. The mixture was diluted with ethyl acetate and quenched with water. The organic layer was extracted several times, washed with brine and dried over anhydrous magnesium sulfate. The dried red solution was concentrated to give 0.100 g (74% yield) red solid. ^1H NMR (CDCl3) δ 7.20 – 6.40 (m, 36H, Ar-H), 5.50 (s, 2H, Cp-H), 4.4 (d, J = 8 Hz, 8H),

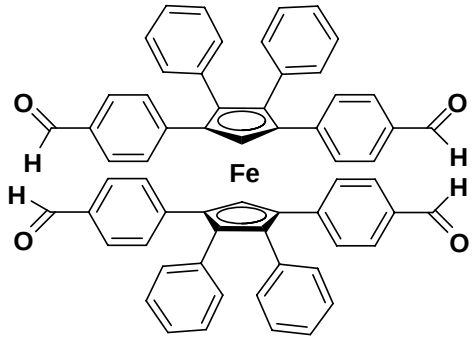
Synthesis of 2,22-Dioxo-10,11,12,13,30,31,32,33-octaphenylferrocenophane (14)



(Bw-6-31, Bw-6-53) A 2-necked flask was charged with calcium hydroxide (0.006 g, 0.073 mmol) and n-Bu_4NHSO_4 (0.005 g, 0.015 mmoles).The materials were vacuumed-flamed dried and maintained under argon. To this was added 5 ml of degassed mixture of water: ethylene chloride (1:1) and 6.0 µL of iron pentacarbonyl with vigorous stirring. A solution of the tetrabromide **13** (0.017 g, 0.015 mmol) in methylene chloride was added to the two phase solution above via canular and the mixture was allowed to stir for 4 hours. Excess active iron reagent was destroyed by bubbling air through the solution for 5 minutes. The mixture was quenched with 1M aqueous HCl and extracted with ethyl acetate several times. The combined organic layer was washed with water, brine, dried over anhydrous sodium sulfate and concentrated to dryness in vacuum. The crude product was subjected to silica gel column

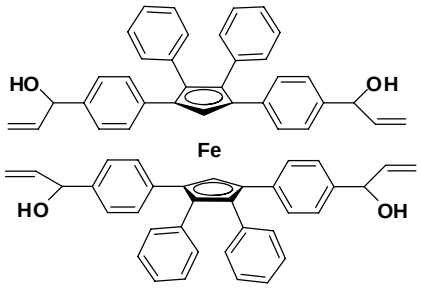
chromatography to give 0.002 g (15% yield) of the material (impure). ^{1}H NMR ($CDCl_3$) δ 7.25 – 6.75 (m, 36 H, Ar-H), 5.50 (s, 2 H, Cp-H), 4.50 (s, 8 H).

Synthesis of 1,4,1',4'-Tetra(4-(formylphenyl]-2,3,2',3'-tetraphenylferrocene (16)



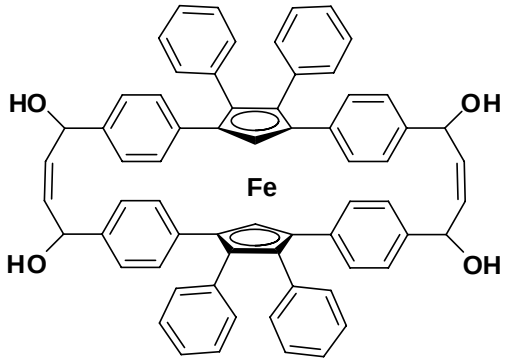
(Bw-7-21, Bw-730) Compound **12** (68 mg, 0.074 mmoles) was dissolved in DMSO with IBX (104 mg, 0.371 mmol). The solution was allowed to stir at room temperature for 3 hours. The mixture was quenched with water and extracted with ethyl acetate several times. The combined organic layer was washed with water, brine and concentrated to dryness. The crude product was subjected to silica-gel column chromatography using gradient mixture of CH_2Cl_2 and ethylacetate mixture as eluant to obtain 67 mg of compound **16** (100% yield).^{1}H NMR ($CDCl_3$) δ 9.90 (s, 4H, CHO), 8.05 (d, J = 8Hz, 1H), 7.99 (d, J = 8Hz, 1H), 7.49 (d, J = 8Hz, 6H), 7.25 (d, J = 8 Hz, 8H), 7.04 (m, 4H), 6.88 (m, 16H), 5.77 (s, 2H, Cp); ^{13}C NMR 191.96, 142.18, 141.96, 134.74, 133.79, 133.37, 132.31, 131.96, 129.73, 129.30, 128.26, 127.61.

Synthesis of 1,4,1',4'-Tetra[4-(1-hydroxy-2-propenyl)phenyl]-2,3,2',3'-tetraphenylferrocene (17)



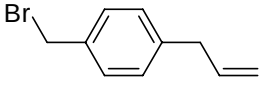
Into a round bottom flask was weighed compound **16** (160 mg, 0.176 mmol) along with a stir bar. The content was vacummed-flammed thoroughly to dry and purged with argon. Dry THF (10 ml) was added to dissolve followed by 1.10 ml of 1M THF solution of vinyl magnesium bromide. The reaction was made to stir at room temperature for 10 hours. The resulting mixture was quenched with aqueous ammonium chloride and extracted with ethyl acetate several times. The combined organic layer was with water, brine, dried over anhydrous sodium sulfate and concentrated to dryness. The crude material was subjected to silica-gel column chromatography using gradient mixture of methylene chloride and ethyl acetate as eluant to obtain 0.116 mg of **17** (65% yield) HRMS (MALDI) m/z 1019.033 (M+1; 100%), 1021.037 (79%, isotope), 1022.040 (29%, isotope); Calcd for $C_{70}H_{58}FeO_4$: ^{1}H NMR (CDCl3) δ 7.12 – 6.80 (m,36H), 6.0 (m, 4H, CH=), 5.6 – 5.0 (m, 14H), 2.2 (bs, 4H, OH); ^{13}C NMR 140.6, 140.4, 10.3, 140.2, 135.2, 135.0, 134.9, 134.6, 132.5, 129.3, 127.1, 126.4, 125.8, 115.3, 115.2, 115.1, 92.2, 85.7, 75.3.

Synthesis of 1,4,22,25-Tetrahydroxy-2,23-diene-11,12,13,14,32,33,34,35-octaphenyl[4.4]ferrocenophane (18)



(Bw-7-24, Bw-7-32) Intermediate **17** (150 mg, 0.148 mmoles) was weighed into a 500-ml round bottom flask along with a stir bar and vacummed-flame dried. Catalytic amounts of second generation Grubbs catalyst (13 mg) was added to the flask in a glove box and sealed. Dry benzene (200 mL) was added and the mixture made to stir at 50^{o}C for 12 hours under constant flow of argon. The solvent was removed under reduced pressure and the residue subjected to silica-gel column chromatography using gradient mixture of methylene chloride and ethyl acetate as eluant to obtain 97 mg of compound **18** (68% yield). MS (MALDI) m/z 962.219 (M^{+}), 963.224 (M+ 1), 964.222 (M + 2). ^{1}H NMR ($CDCl_3$ + CH_3OD) δ 7.2 – 6.7 (m, Ar), 6.06 (s, 4H, =CH), 5.79 (s, 2H, Cp), 4.73 (bs, 4H, CHO).

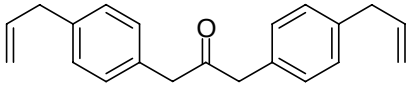
Synthesis of 1-allyl-4-(bromomethyl) benzene (33)



(Bw-7-56, Bw-7-93) To a round bottom flask was added 8.0 g (30.31 mmol) of the dibromide **2** and dried thoroughly with a heat gun under vacuum. Mixture of ether/THF (160 mL) in 1:1 ratio was added under argon. To the above mixture were added 31 mL of 1.0 M THF solution of vinyl magnesium bromide (30.31 mmol) and 5.3 mL (30.31 mmol) of HMPA. The reaction was allowed to stir at room temperature for 24 hours. The reaction was quenched with saturated

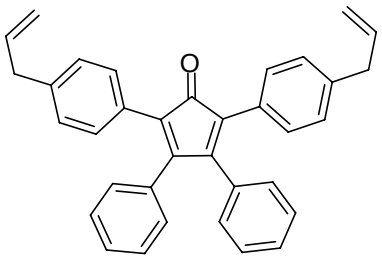
aqueous NH_4Cl solution and the organic layer extracted with ether. The organic layer was washed with brine, dried over anhydrous sodium sulphate, filtered and concentrated to dryness. The crude product was purified by column chromatography on silica gel using a gradient mixture of hexane and diethyl ether as eluant to give 2.4 g (54% yield) of **33** after recovering 2.4 g (30%) of starting material**.** ^{1}H NMR ($CDCl_3$) δ 3.30 (d, J = 6.6 Hz, 2H, Ar-CH_2-C=), 4.37 (s, 2H, Ar-CH2-Br), 5.00 (d, J = 13.8 Hz, 2 H, =CH_2), 5.90 (m, C-CH=C, 7.09 (d, J = 5.8 Hz, 2H, Ar-H), 7.23 (d, J = 6.6 Hz, 2H, Ar-H) ; ^{13}C NMR (CDCl3) δ 140.38, 136.99, 135.59, 129.17, 129.01, 116.17, 39.91, 33.63.

Synthesis of 1,3-bis(4-allylphenyl)propan-2-one (34)



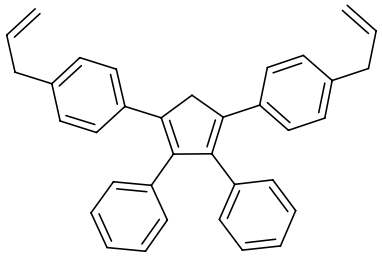
(Bw-7-99, Bw-8-41) A 2-necked flask was charged with $Ca(OH)_2$ (1.96 g, 26.53 mmol) and 1.13 g (3.32 mmol) of n-Bu_4NHSO_4. The flask with its content was vacuum-flamed thoroughly to dry and maintained under argon. Mixture of degassed water/ methylene (100 mL) in 1:1 ratio was added. Argon was bubbled through the solution for 5 minutes and 1.0 mL of iron pentacarbonyl was added with vigorous stirring. A solution of **33** (2.80 g, 13.27 mmol) in methylene chloride was added to the reaction mixture via canular. Reaction was allowed to stir vigorously at room temperature for 3 hours. Air was bubbled through the reaction to destroy excess $Fe(CO)_5$. The resulting mixture was filtered through a sintered glass. The filtrate was quenched with dilute aqueous hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with water, brine, dried over anhydrous sodium sulfate, filtered and concentrated to dryness. The crude product was subjected to silica gel column chromatography using gradient mixture of hexane/diethyl ether as eluant to give 1.15 g (60% yield) of **34.** MS (HRMS TOF ES) m/z 291.1747 (M + 1), Calcd 291.1749 (M + 1); ^{1}H NMR δ 7.11 (d, J = 3.2 Hz, 8H, Ar-H), 5.90(m, 2H, C-CH=C), 5.10 (dd, J = 11.6 Hz, 15.6 Hz, 4H, 2 =CH_2), 3.66 (s, 2Ar-CH_2-CO), 3.36 (d, J = 6.6 Hz, 4H, 2 Ar-CH_2-C=); ^{13}C NMR ($CDCl_3$) δ 206.17, 139.04, 137.49, 131.91, 129.73, 129.11, 116.07, 48.85, 40.02

Synthesis of 2,5-Bis(4-allylphenyl)-3-,4-diphenylcyclopenta-2,4-dienone (35).



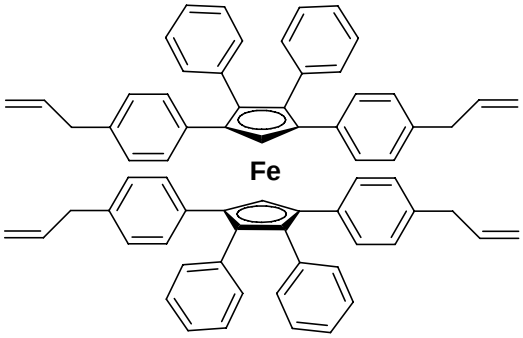
(Bw-7-71, Bw-7-79, HZ-10-19) To a solution of 0.66 g of **34** (2.26 mmoles) in dry distilled ethanol (20 mL) was added 0.32 ml (2.26 mmoles) of DBU. The mixture was stirred at room temperature for 30 minutes. An ethanol solution of benzil (0.48 g, 2.26 mmoles) was added via canular. The mixture was stirred at room temperature for 12 hours. The ethanol was removed by rotary evaporator and the crude product quenched with aqueous ammonium chloride and extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous sodium sulfate and concentrated to dryness to obtain a dark purple solid. The crude was treated with pyridine and thionyl chloride at 0^{o}C for 30 minutes. Reaction was quenched with aqueous ammonium chloride and extracted with ethylacetate.The organic layer was washed with water, brine, dried over anhydrous sodium sulfate and concentrated to dryness. This was subjected to silica gel column chromatography using hexane / ether mixture as eluant to yield 0.73 g (70% yield) of **35** which is a solid with a dark purple color. MS (HRMS TOF ES) m/z 465.2215 (M + 1), 487.2012 (M + Na), calcd. 465.2218 (M + 1), 487.2012 (M + Na); ^{1}H NMR δ 3.34 (d, J = 6.6 Hz, 4H), 5.10 (dd, J = 11.0 Hz,17.3 Hz, 4H, 2 Ar-CH_2-C=), 5.88 – 5.95 (m, 2H, 2 C-CH=C), 6.85-7.25 (m, 18H, Ar-H); ^{13}C NMR (CDCl3) δ 200.00, 154.27, 139.55, 137.34, 133.50, 130.39, 129.51, 128.57, 128.47, 128.17, 125.69, 125.25, 116.12, 40.00.

Synthesis of 1-Allyl-4-(4-(4-allylphenyl)-2,3-diphenylcyclopenta-1,3-dienyl)benzene (36)



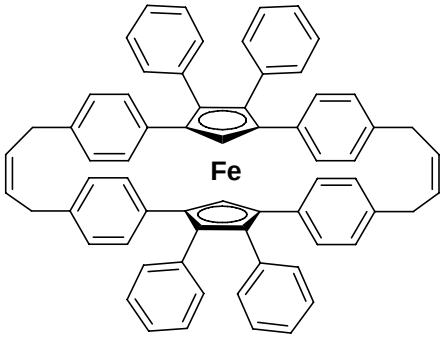
(Bw-7-72) An ethereal solution of compound **35** (0.40 g, 0.86 mmoles) in a two-necked round bottom flask was added $AlCl_3$ (240 mg, 1.80 mmol) and $LiAlH_4$ (65 mg, 1.72 mmol) at 0^oC.The purple color was immediately discharged to give a yellowish-green solution which was put to reflux at 35^oC for 4 hours. The mixture was quenched with iced cold water and extracted with ether. The organic layer was washed with water, brine and dried over anhydrous sodium sulfate. The ethereal solution was concentrated to dryness and subjected to silica-gel column chromatography using hexane and diethyl ether mixture as eluant to obtain 0.325 g of compound **36** (84.0% yield). ^1H NMR (CDCl3) δ 6.97 – 7.12 (m, Ar-H, 18H), 5.88 – 5.95 (m, 2H, 2 C-CH=C), 5.01 (dd, J = 11.0 Hz,17.3 Hz, 4H, 2 C=CH_2), 3.98 (s, 2H), 3.30 (d, J = 6.8 Hz, 4H); ^{13}C NMR (CDCl3) δ 144.37, 139.45, 138.32, 137.45, 136.96, 134.48, 129.99, 128.52, 128.23, 127.95, 126.79, 116.02, 46.00, 40.00.

Synthesis of 1,4,1',4'-Tetra[4-(1-propenyl)phenyl]-2,3,2'3'-tetraphenylferrocene (37):



(Bw-7-77) The intermediate **36** (0.325 g,0.721 mmoles) was weighed into a two-necked round bottom flask along with a stir bar with an attached glass delivery tube. Iron(II) chloride (91 mg, 0.721 mmol) was weighed into a small round bottom flask in a glove box and attached to the delivery tube. The above setup was thoroughly vacummed-flammed dried and purged with argon. 5.0 ml of dry THF was added to dissolve compound **36** with subsequent addition of 0.68 ml of 1.2M of n-butyl lithium at -78^{o}C. The resulting dark blue solution was stirred for one hour. The iron(II) chloride was transferred into the solution through the delivery tube and the reaction made to warm to room temperature for 12 hours. The mixture was diluted with ethyl acetate and quenched with aqueous ammonium chloride. The organic layer was extracted, washed with brine, dried over anhydrous sodium sulfate and concentrated to dryness. The crude product was subjected to silica-gel column chromatography to obtain 0.309 g of **37** (90 % yield). ^{1}H NMR δ 6.78 – 7.06 (m, Ar-H, 36 H), 5.88 – 5.95 (m, 4 H, CH=C), 5.44 (s, Cp-H, 2H), 5.01 (dd, J = 11.0 Hz, 17.3 Hz, 8H, C=CH_2), 3.28 (d, J = 6.4 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 138.15, 137.67, 135.40, 133.33, 132.51, 129.39, 127.95, 126.99, 126.27, 115.82, 91.45, 86.07, 67.89, 40.13

Synthesis of 2,23-Diene-11,12,13,14,32,33,34,35-octaphenyl[4.4]ferrocenophane (22)

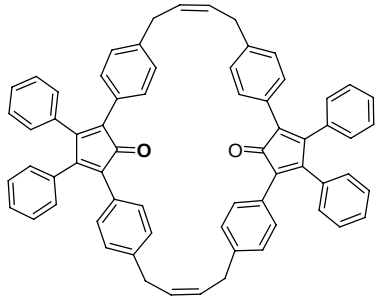


(Bw-7-68, 75) Ferrocene **37 (**0.202 g, 0.211 mmoles) was weighed into a 500-ml round bottom flask along with a stir bar and vacummed-flammed to dry. To this was added 0.018 g of second generation Grubbs catalyst in a glove box and sealed. Dry benzene (200 mL) was added and the mixture made to stir at 50^{o}C for 12 hours. The solvent was removed under reduced pressure and collected for re-use. The residue was subjected to silica-gel column chromatography using methylene chloride and hexane mixture as eluant to obtain 0.133g of **22** (70 % yield). ^{1}H NMR

($CDCl_3$) δ 7.5 – 6.5 (m, 36 H, Ar-H), 5.75 – 5.45 (m, 4H), 5.2 (s, 2 H, Cp-H), 3.3 (d, J = 6.8 Hz, 8 H)

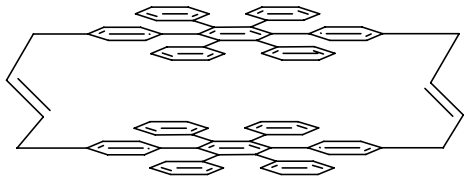
Experimental methods for Chapter 3

Synthesis of Cyclopentadienone 41



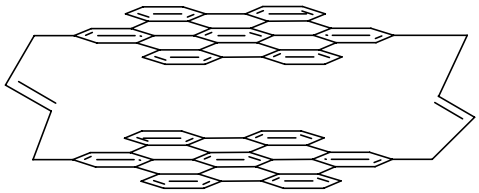
(Bw-8-33, Bw-8-67) The cyclopentadienone **35** (0.04g, 0.086 mmoles) was weighed into a round bottom flask and vacuum dried thoroughly. Catalytic amount of second generation Grubbs catalyst (8 mg, 0.009 mmol) was added in a glove box. Freshly distilled benzene (250 mL) was added via canular.The reaction mixture was allowed to stir at 60^{o}C for 3 days and the benzene distilled off under reduced pressure. The residual solid was subjected to silica gel column chromatography employing hexane/methylene chloride/ isopropyl ether mixture as eluant to obtain 0.016g of compound **41** (43% yield). MS (HRMS TOF ES) m/z 890.4018 (M + NH_4), 895.3580 (M + Na), calc. 890.3998 (M + NH_4), 895.3552 (M + Na); ^{1}H NMR δ 6.83- 7.25 (m, 36 H, Ar-H), 5.64 (t, J = 8 Hz, 4H), 3.27 (d, J = 4.2 Hz, 8 H); ^{13}C NMR ($CDCl_3$) δ 200.00, 153.36, 140.39, 133.74, 131.23, 130.44, 129.51, 128.36, 128.15, 125.14, 28.21.

Synthesis of 2,24-Diene-12,13,15,16,34,35,37,38-octaphenyl[4.4.]triphenylophane (46)



(Bw-7-113, Bw-8-63) The cyclopentadienone **41** (0.015 g, 0.017 mmoles) was weighed into a round bottom flask along with a stir bar. Into this was added diphenylacetylene (0.004g, 0.023 mmoles).The mixture was dissolved in 3 mL of diphenyl ether and the resulting solution was refluxed for 12 hours .The purple color was discharged to give a pale yellowish solution. The solvent was distilled off under vacuum. The remaining residue subjected to silica gel column chromatography using hexane/diethyl ether solvent system as eluant to give 0.008 g of the coronene **46** (40% yield). MS (HRMS TOF ES+) m/z 1195.5183 (M + Na), calc. 1195.5219 (M + Na); ^{1}H NMR δ 6.65 – 7.01 (m, Ar-H, 56H), 5.38 (t, J = 4Hz, 4H), 2.99 (d, J = 6 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 140.96, 140.66, 138.21, 137.48, 133.29, 131.73, 130.93, 130.02, 127.09, 126.56, 125.38, 38.05.

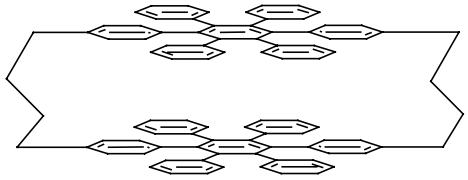
Synthesis of 2,36-Diene[4.4]hexa-peri-hexabenzocoronenophane (47)



(Bw-8-40, 71, Bw-8-89) A solution of compound **46** (0.0048 g, 0.0041 mmol) in methylene chloride was added to a stirred solution of $FeCl_3$ (0.027g, 0.164 mmoles) in nitromethane (0.7 ml) .A stream of argon was continuously bubbled through the reaction mixture for 24 hours at room temperature. The reaction was quenched with aqueous sodium bicarbonate and extracted with chloroform. The organic layer was washed with brine and dried over anhydrous magnesium sulfate and concentrated to dryness under reduced pressure. The crude material was subjected to

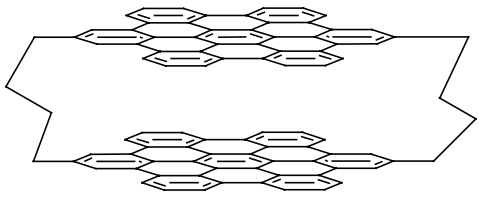
silica gel column chromatography using a mixture of chloroform and hexane/ toluene to obtain **47** (2 mg, 50% yield). ^{1}H NMR δ 7.8 – 8.5 (m, Ar-H, 32 H), 5.5 (t, J = 4 Hz, 4H), 1.99 (d, J = 6 Hz, 8 H). This compound has not been fully characterized due to limited amount of material.

Synthesis of 12,13,15,16,34,35,37,38-Octaphenyl[4.4]triphenylophane (48)



(Bw-8-90) The cyclophane **46** (5 mg, 0.004 mmol) was made to dissolve in ethanol. To this was added 10.0 mg of 10% Pd/C under 1 atmosphere of hydrogen. This was allowed to stir at ambient temperature for 6 hours. The solution was filtered through celite and the filtrate concentrated to dryness under vacuum. The crude residue was subjected to silica gel column chromatography to obtain **48** (0.004g, 80% yield). ^{1}H NMR δ 7.00 – 6.02 (m, 56 H, Ar-H), 2.31 (bs, 8 H, Ar-CH_2-), 1.38 (bs, 8 H, -CH_2-); ^{13}C NMR ($CDCl_3$) δ 141.11, 140.69, 137.89, 137.58, 134.00, 131.89, 128.50, 128.00, 125.44, 33.37, 26.06.

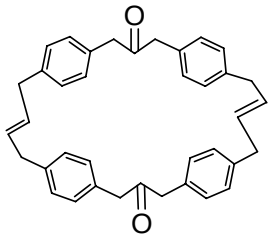
Attempted synthesis of [4.4]Hexa-peri-hexabenzocoronenophane (49)



(Bw-8-40, 71) To a solution of $FeCl_3$ (0.004g, 0.2727 mmol) in nitromethane was added the cyclophane **48** (8 mg, 0.007 mmoles) in methylene chloride and the solution made to stir at room temperature. Argon was bubbled through the reaction for 18 hours. Thin layer chromatograph

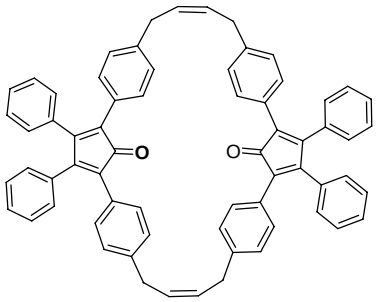
indicated no starting material. The reaction was quenched with aqueous dilute hydrochloric acid (10 %) and extracted with chloroform several times. The combined organic layer was washed with brine, and concentrated to dryness. Material has not been characterized. Reaction conditions needs to be optimized to improve yield and scaled up.

Synthesis of 2,21-Dioxo-11,30-diene[3.4.3.4]paracyclophane (53)



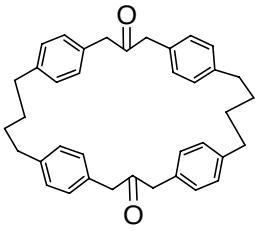
(Bw-8-53, Bw-8-63, 55,73, Bw-8-88) The intermediate **34** (0.100g, 0.344 mmol) was weighed into a round bottom flask and thoroughly vacuumed-flame dried. Catalytic amount of second generation Grubbs catalyst (0.015g, 0.017 mmoles) was added to the flask in a glove box. Distilled methylene chloride (300 mL) was added to the flask via canular. The mixture was allowed to stir at 60 ^{0}C for 12 - 18 hours. The methylene chloride was removed in vaccuo (under reduced pressure) and collected to be re-used. The crude material was then subjected to silica gel column chromatography using hexane and diethyl ether mixture as eluting solvent to give 0.040 g of the cyclophane **53** in 60% yield after 0.025 g of recovered starting material. MS (HRMS TOF ES) m/z 547.2629 (M + Na), calc. 547.2613 (M + Na); ^{1}H NMR δ 7.00 – 7.13 (m, Ar-H); 5.59 – 5.65 (m, -CH=CH-); 3.68 (s, Ar-CH_2-CO), 3.34 (d, J = 5.2 Hz, Ar-CH_2-C=); ^{13}C NMR ($CDCl_3$) δ 206.10, 139.53, 131.84, 130.60, 129.68, 129.12, 48.69, 38.63

Alternative synthetic approach to 41



(Bw-8-61, 67)The macrocyclic diketone **53** (0.058 g, 0.109 mmol) was weighed into a round bottom flask along with a magnetic stir bar and dried thoroughly. 15mg of potassium hydroxide and benzil (0.057g, 0.272 mmoles) were then weighed out and added to the flask. The flask and its content were vacuumed -dried and purged with an inert gas. Dried ethanol (5mL) was added and the reaction brought to reflux for 5 hours. Ethanol was removed in under vacuum and the crude residue subjected to silica gel column chromatography employing a mixture of hexane and methylene chloride as eluting solvents to afford 0.045g (96 % yield) of **41** as a brightly colored fine purple powder. ^{1}H NMR δ 6.83- 7.25 (m, 36H, Ar-H), 5.64 (t, J = 6.6 Hz, 4H), 3.27 (d, J = 4.2 Hz, 8H); ^{13}C NMR (CDCl3) δ 200.00, 153.36, 140.39, 133.74, 131.23, 130.44, 129.51, 128.36, 128.15, 125.14, 28.21

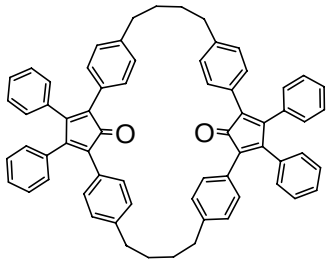
Synthesis of 2,21-Dioxo[3.4.3.4]paracyclophane (54)



(Bw-8-91) An ethanolic solution of the diketone cyclophane, **53** (0.050 g, 0.095 mmol) was weighed into a 2-necked round bottom flask along with a stir bar. To this was added 50.0 mg of

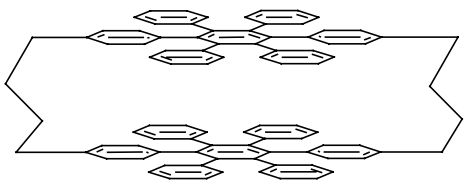
10 % Pd/C and the reaction made to stir at room temperature under 1 atm. of hydrogen gas for 2 hours. The solution was filtered through celite and concentrated to dryness. The crude product was purified by silica gel column chromatography to obtain **54** (0.045 g, 100 % yield). ^{1}H NMR δ 7.01 (d, J = 8 Hz, Ar-H, 8 H), 6.93 (d, J = 8 Hz, Ar-H, 8 H), 2.58 (bt, 8 H), 1.54 (t, J = 3 Hz, 8 H); ^{13}C NMR ($CDCl_3$) δ 206.53, 141.21, 131.43, 129.60, 128.96, 48.79, 35.45, 30.47

Synthesis of Cyclopentadienone (55)



(Bw-8-96, MT-2-22) Into a round bottom flask was weighed the diketone **54** (0.045 g, 0.085 mmol), benzil (0.036 g, 0.170 mmoles). To this was added 9.0 mg of potassium hydroxide and the content vacuumed thoroughly to dry. Dry ethanol (10.0 ml) was added to the mixture and the solution brought to reflux for 6 hours. The reaction was quenched with aqueous sodium bicarbonate and extracted into methylene chloride. The organic layer was washed several times with water dried over anhydrous sodium sulfate and concentrated to dryness. After purification with silica gel column chromatography, 0.030 g of **55** (40 % yield) was obtained. ^{1}H NMR δ 1.54 (t, J = 3 Hz, 8 H), 2.58 (bt, 8 H), 6.93 – 7.01 (m, Ar-H, 36 H).

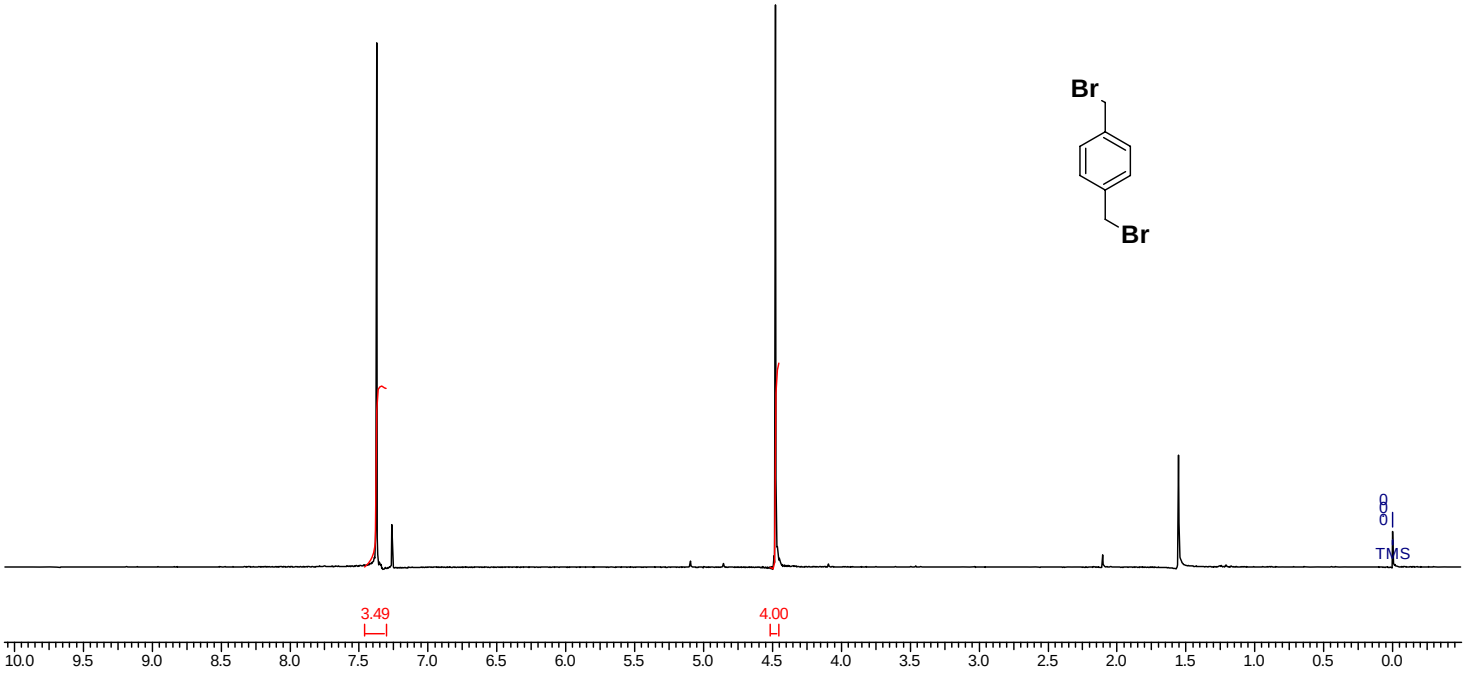
Alternative synthetic approach to Triphenylophane (48)



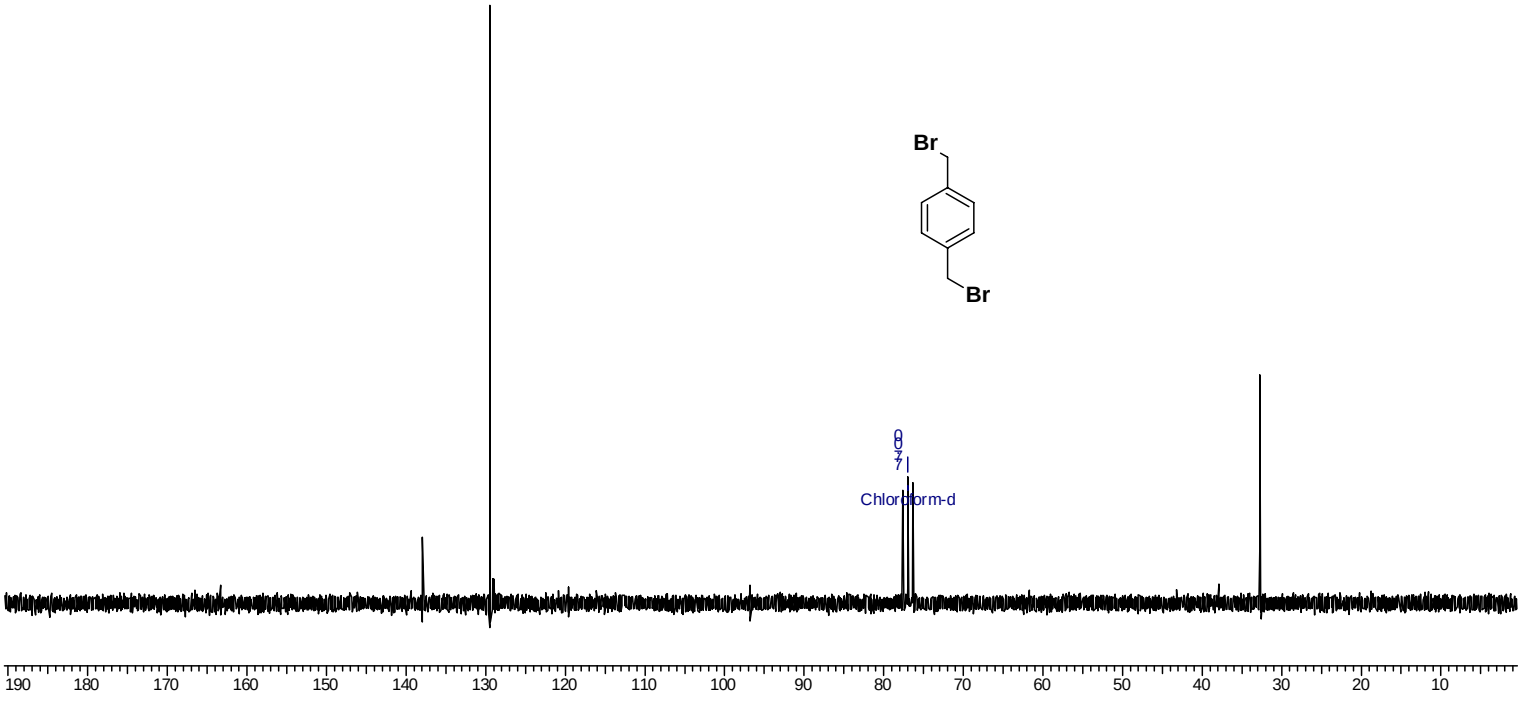
(Bw-8-98, MT-2-23) The cyclopentadienone **55** (0.010 g, 0.011 mmol) was weighed into a round bottom flask along with a stir bar. Into this was added diphenylacetylene (0.010g, 0.057 mmoles) and the mixture dissolved in 2 mL of diphenyl ether. The resulting solution was heated at 260^{o}C to reflux for 12 hours. The purple color was discharged to give a pale yellowish solution. The solvent was distilled off under vacuum. The remaining residue was subjected to silica gel column chromatography using hexane/diethyl ether solvent system as eluants to give 0.005 g of the coronene **48** (38% yield). ^{1}H NMR δ 7.00 – 6.02 (m, 56 H, Ar-H), 2.31 (bs, 8 H, Ar-CH_2-), 1.38 (bs, 8 H, -CH_2-); ^{13}C NMR (CDCl3) δ 141.11, 140.69, 137.89, 137.58, 134.00, 131.89, 128.50, 128.00, 125.44, 33.37, 26.06.

Appendix A - ^{1}H and ^{13}C NMR for Chapter 2

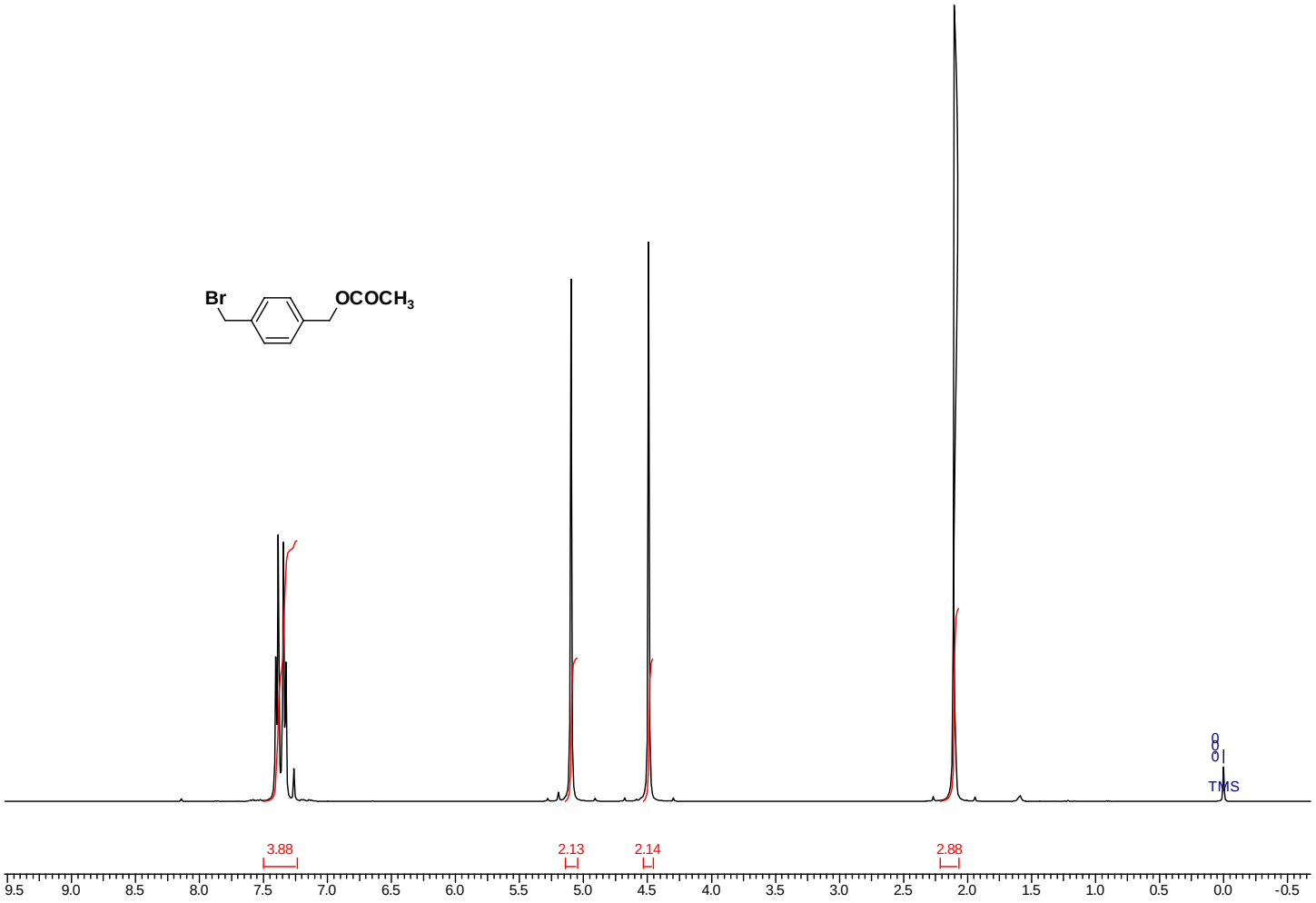
Acquisition Time (sec)	2.7304	***Comment***	STANDARD 1H OBSERVE			***Date***	Aug 31 2006
Frequency (MHz)	199.98	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	5984
Solvent	CDCl3	***Sweep Width (Hz)***	3000.30	***Temperature (grad C)***	29.000		



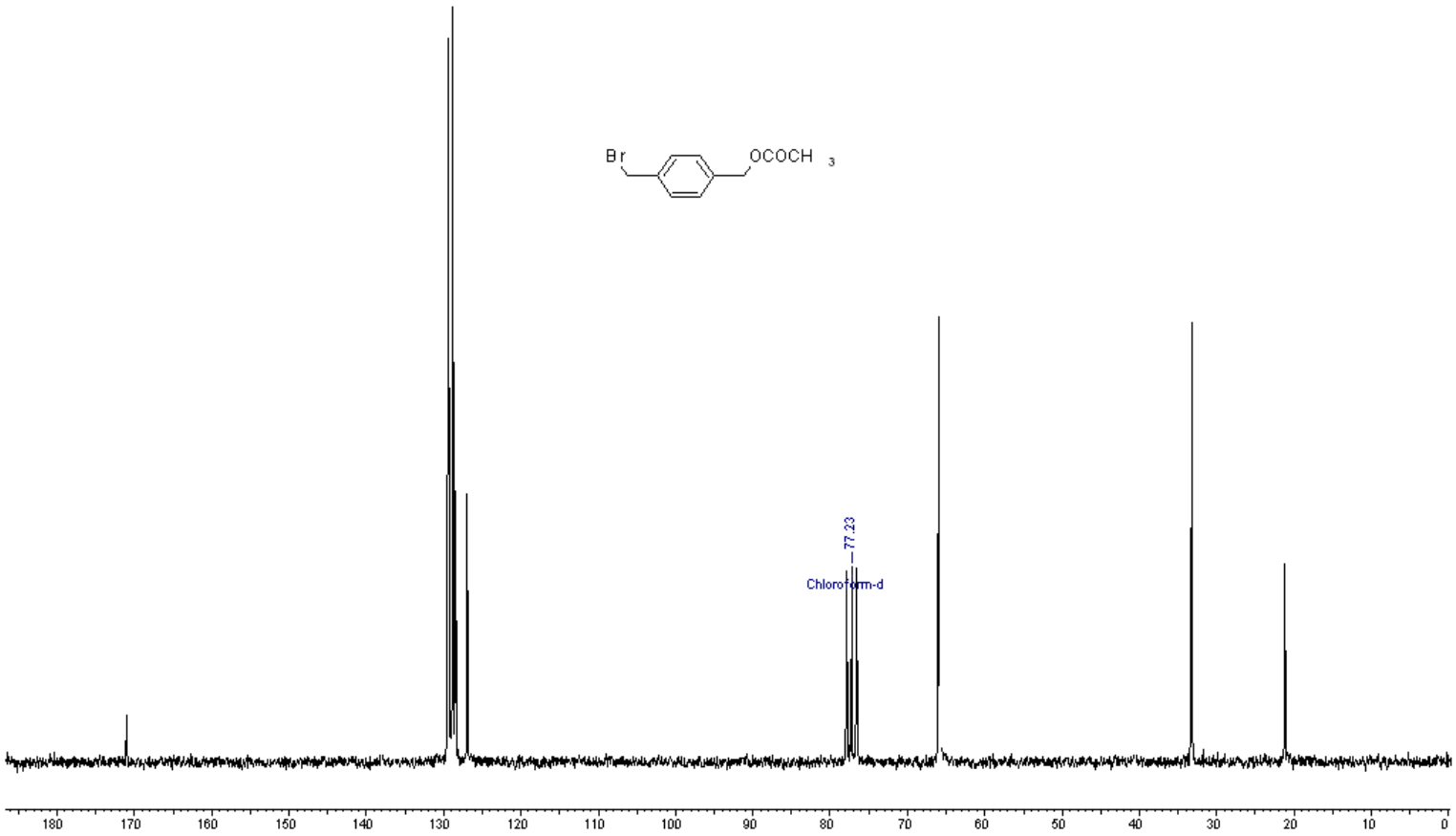
Acquisition Time (sec)	2.6214	***Comment***	13C OBSERVE			***Date***	Aug 12 2007
Frequency (MHz)	50.29	***Nucleus***	13C	***Original Points Count***	18720	***Points Count***	32768
Sweep Width (Hz)	12500.00			***Temperature (grad C)***	29.000		



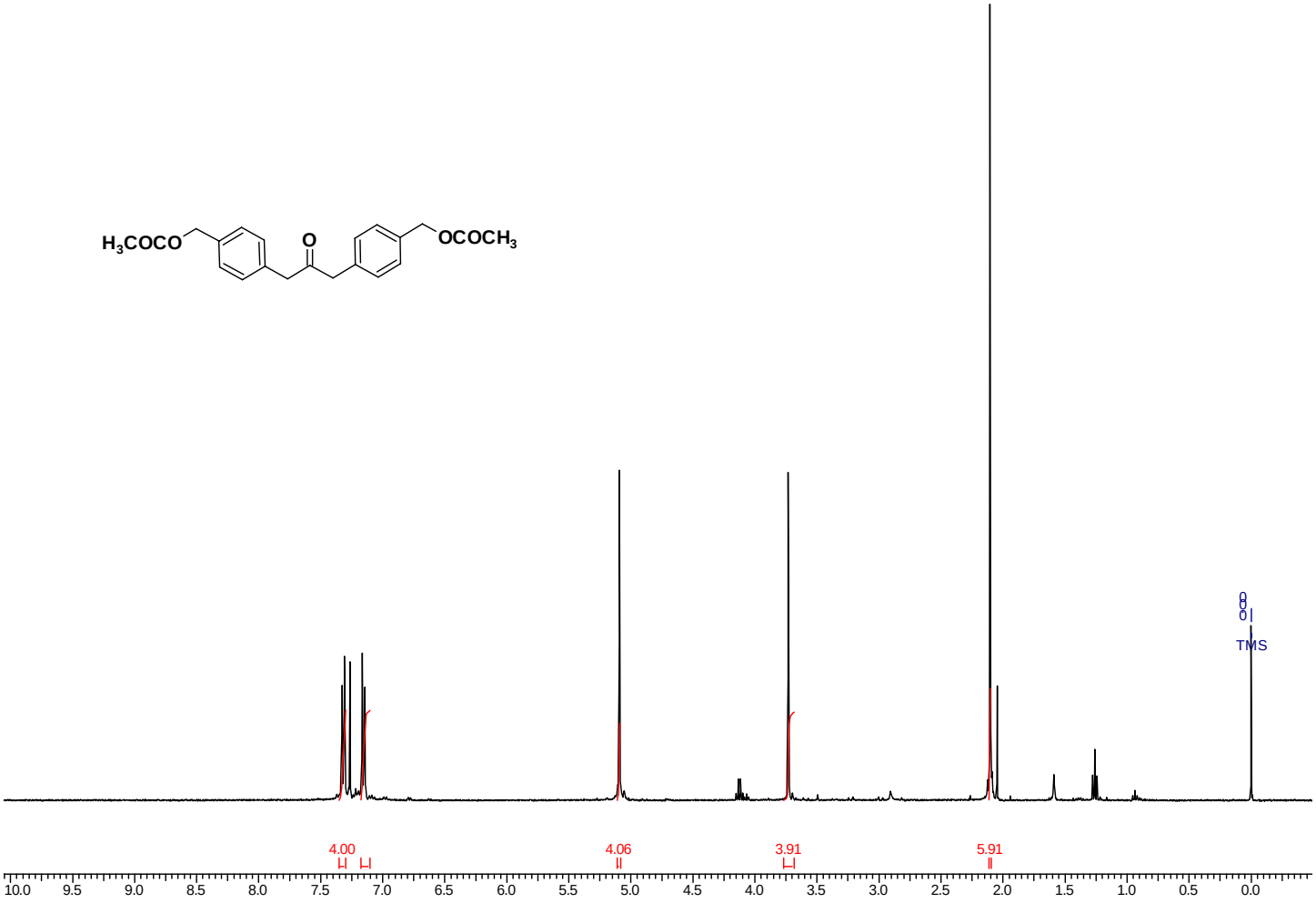
Acquisition Time (sec)	5.4608	***Comment***	STANDARD 1H OBSERVE			***Date***	Jan 31 2005
Frequency (MHz)	399.80	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	22208
Solvent	CDCl3	***Sweep Width (Hz)***	6000.60	***Temperature (grad C)***	29.000		



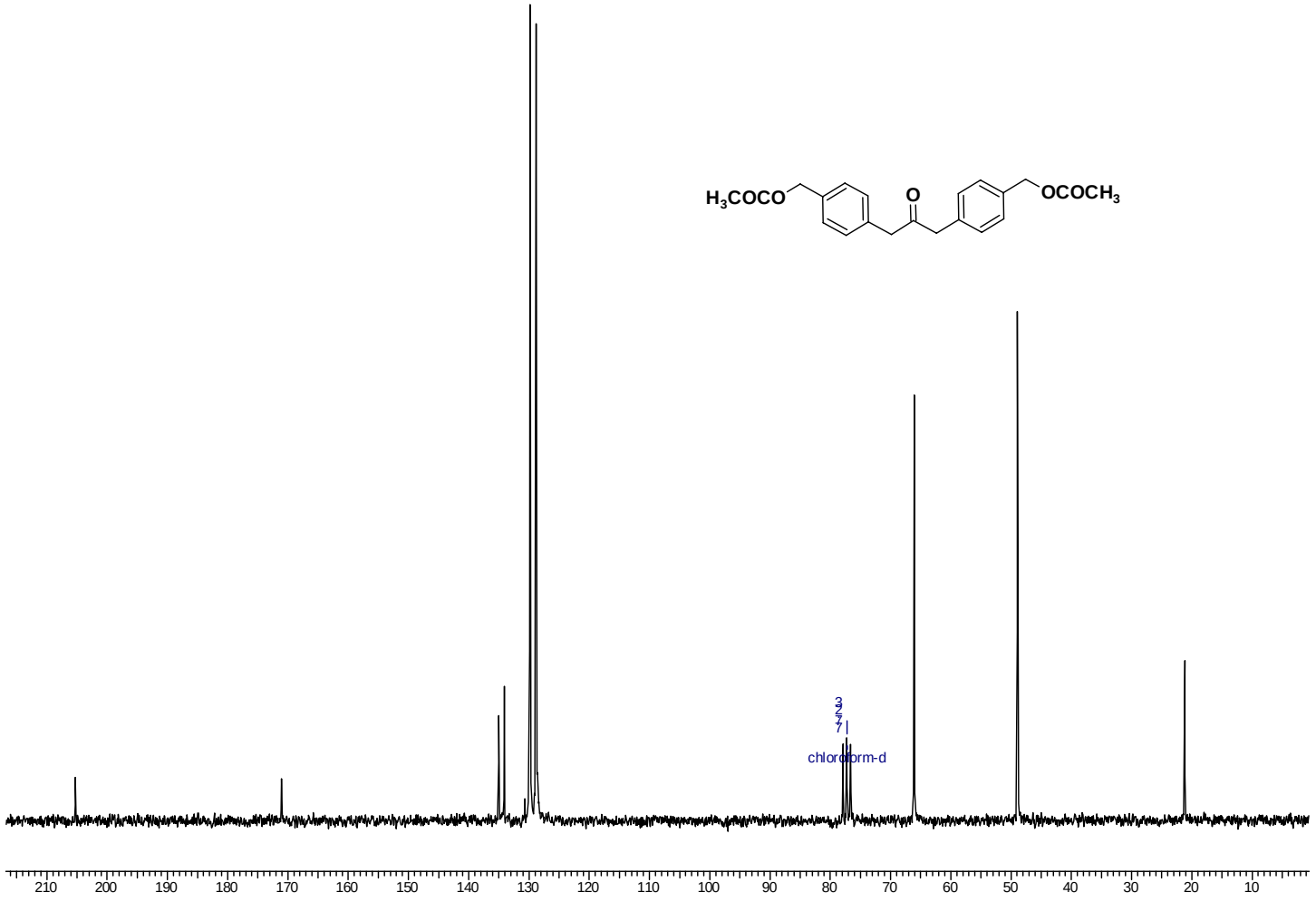
Acquisition Time (sec)	2.6214	Comment	13C OBSERVE		Date	Nov 23 2008	
Frequency (MHz)	50.29	Nucleus	13C	Number of Transients 10000	Original Points Count	18720	Points Count 32768
Solvent	CDCl3	Sweep Width (Hz)	12500.00		Temperature (grad C)	29.000	



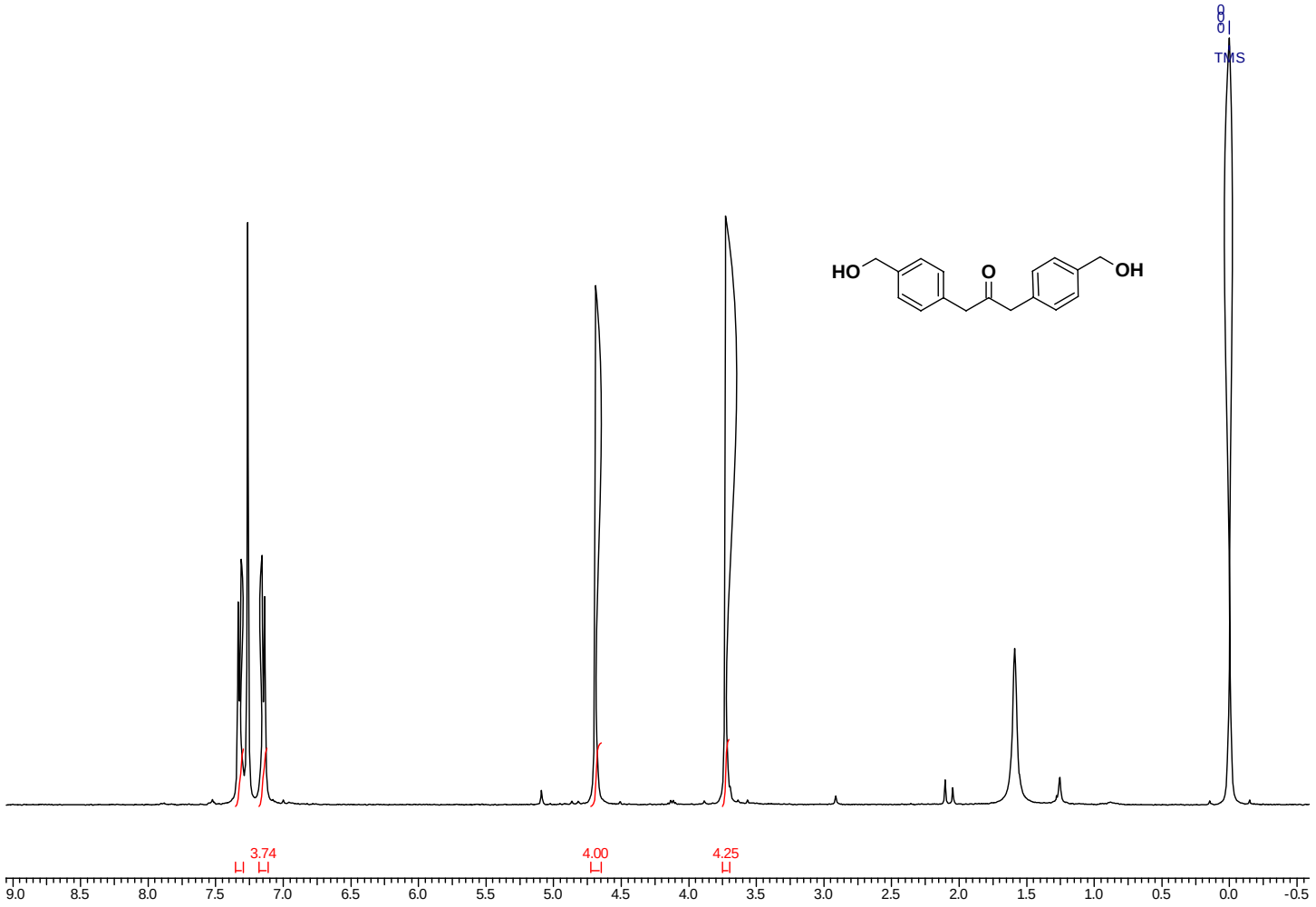
Acquisition Time (sec)	5.4608	***Comment***	STANDARD 1H OBSERVE			***Date***	Mar 23 2005
Frequency (MHz)	399.80	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	22208
Solvent	CDCl3	***Sweep Width (Hz)***	6000.60	***Temperature (grad C)***	29.000	***Points Count***	32768



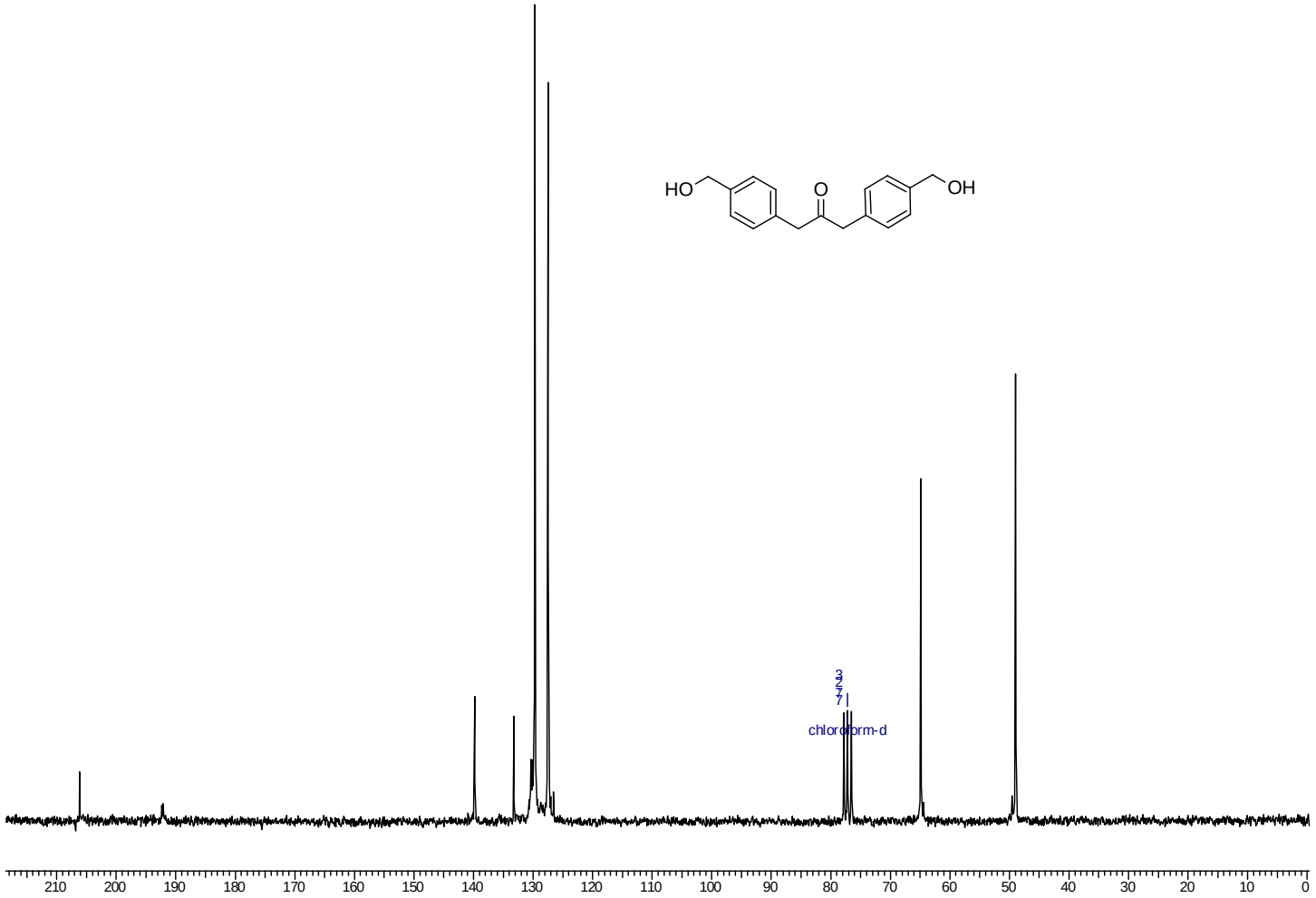
Acquisition Time (sec)	2.6214	***Comment***	13C OBSERVE		***Date***	Oct 11 2007	
Frequency (MHz)	50.29	***Nucleus***	13C	***Number of Transients*** 1000	***Original Points Count***	18720	***Points Count*** 32768
Solvent	CDCl3	***Sweep Width (Hz)***	12500.00		***Temperature (grad C)***	29.000	



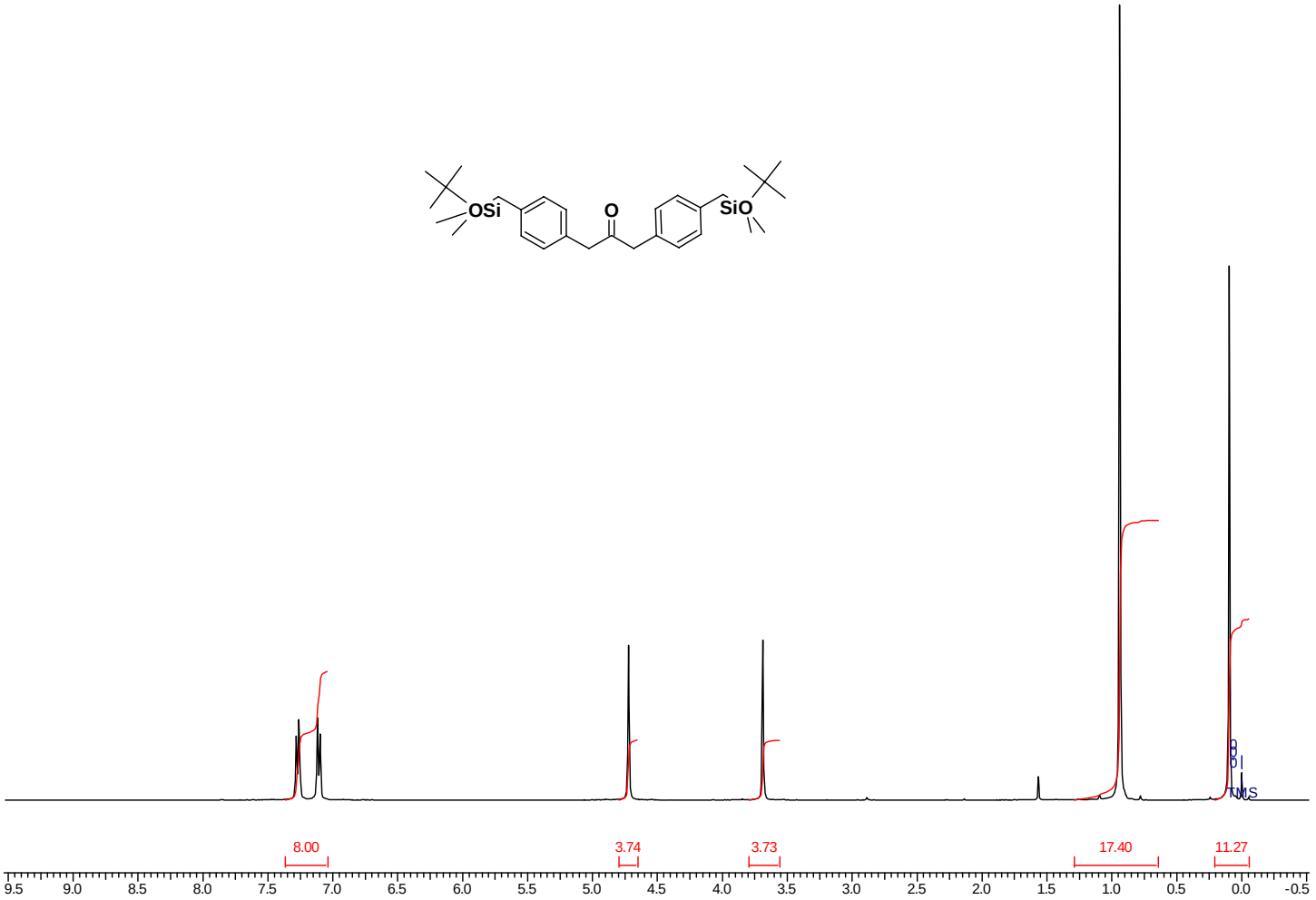
Acquisition Time (sec)	5.4608	***Comment***	STANDARD 1H OBSERVE			***Date***	Feb 14 2005
Frequency (MHz)	399.80	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	22208	***Points Count***	32768
Solvent	CDCl3	***Sweep Width (Hz)***	6000.60	***Temperature (grad C)***	29.000				



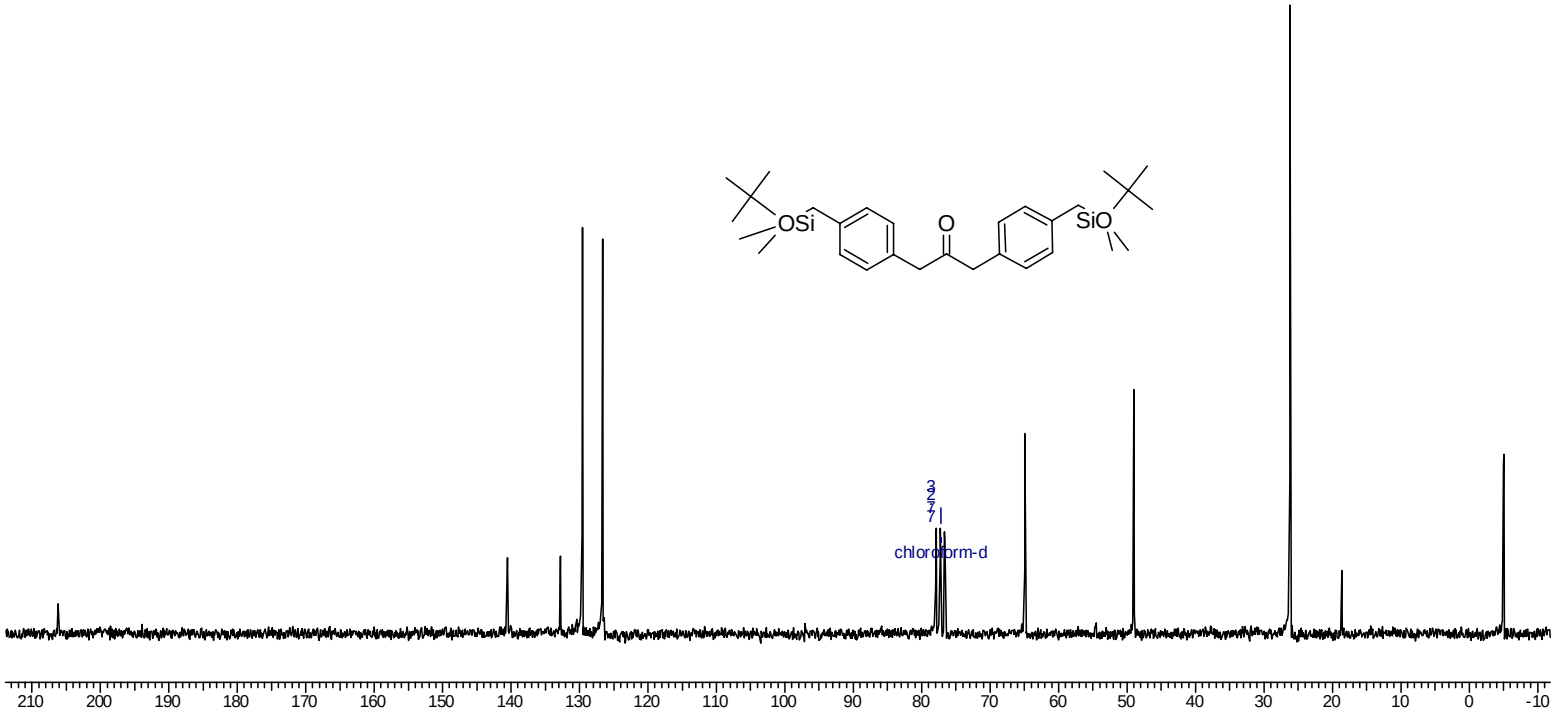
Acquisition Time (sec)	2.6214	***Comment***	13C OBSERVE		***Date***	Jul 25 2006	
Frequency (MHz)	50.29	***Nucleus***	13C	***Number of Transients*** 2000	***Original Points Count***	18720	***Points Count*** 32768
Solvent	CDCl3	***Sweep Width (Hz)***	12500.00		***Temperature (grad C)***	29.000	



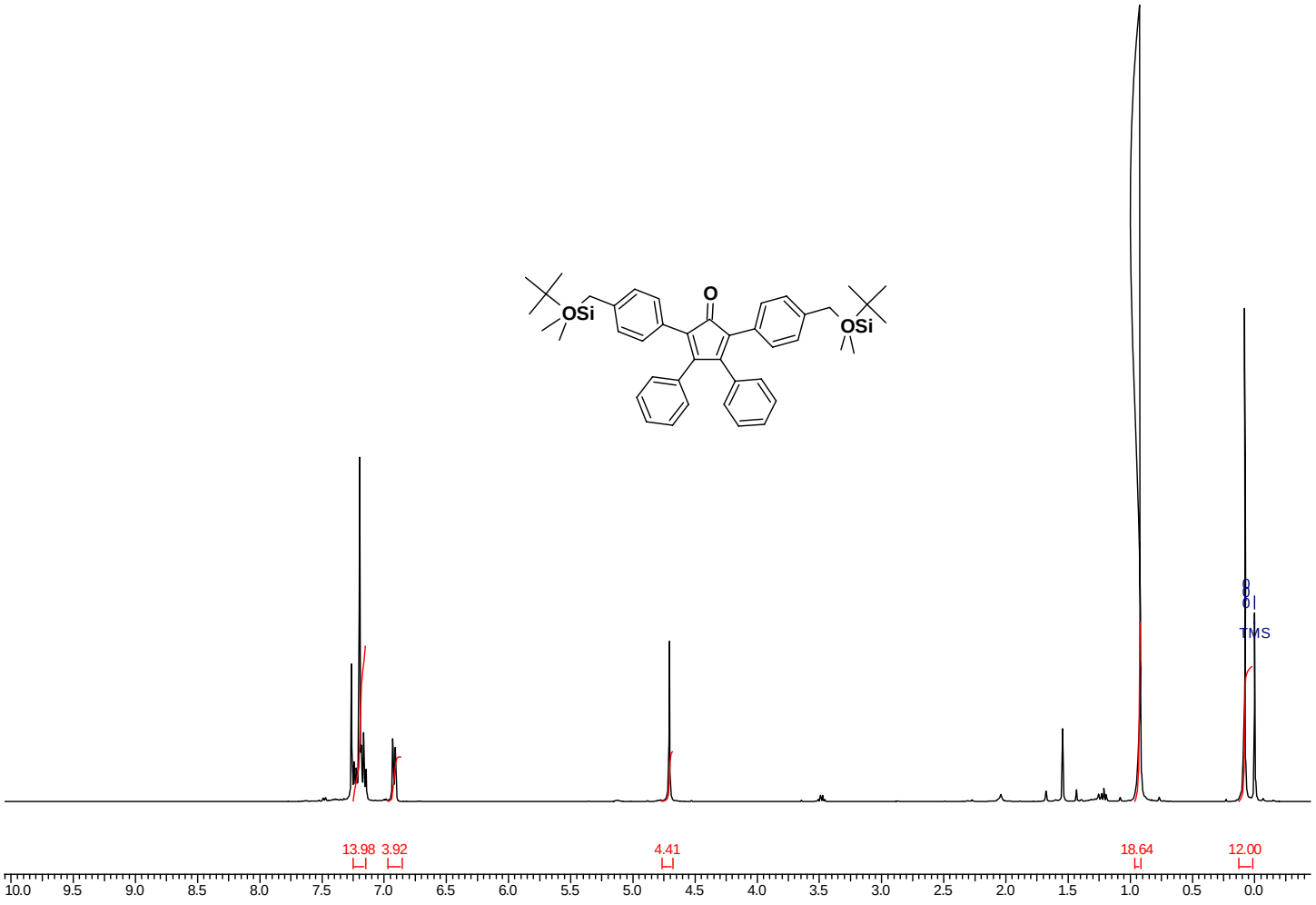
Acquisition Time (sec)	5.4608	***Comment***	STANDARD 1H OBSERVE			***Date***	Jun 30 2005
Frequency (MHz)	399.79	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	22208	***Points Count***	32768
Solvent	CDCl3	***Sweep Width (Hz)***	6000.60	***Temperature (grad C)***	29.000				



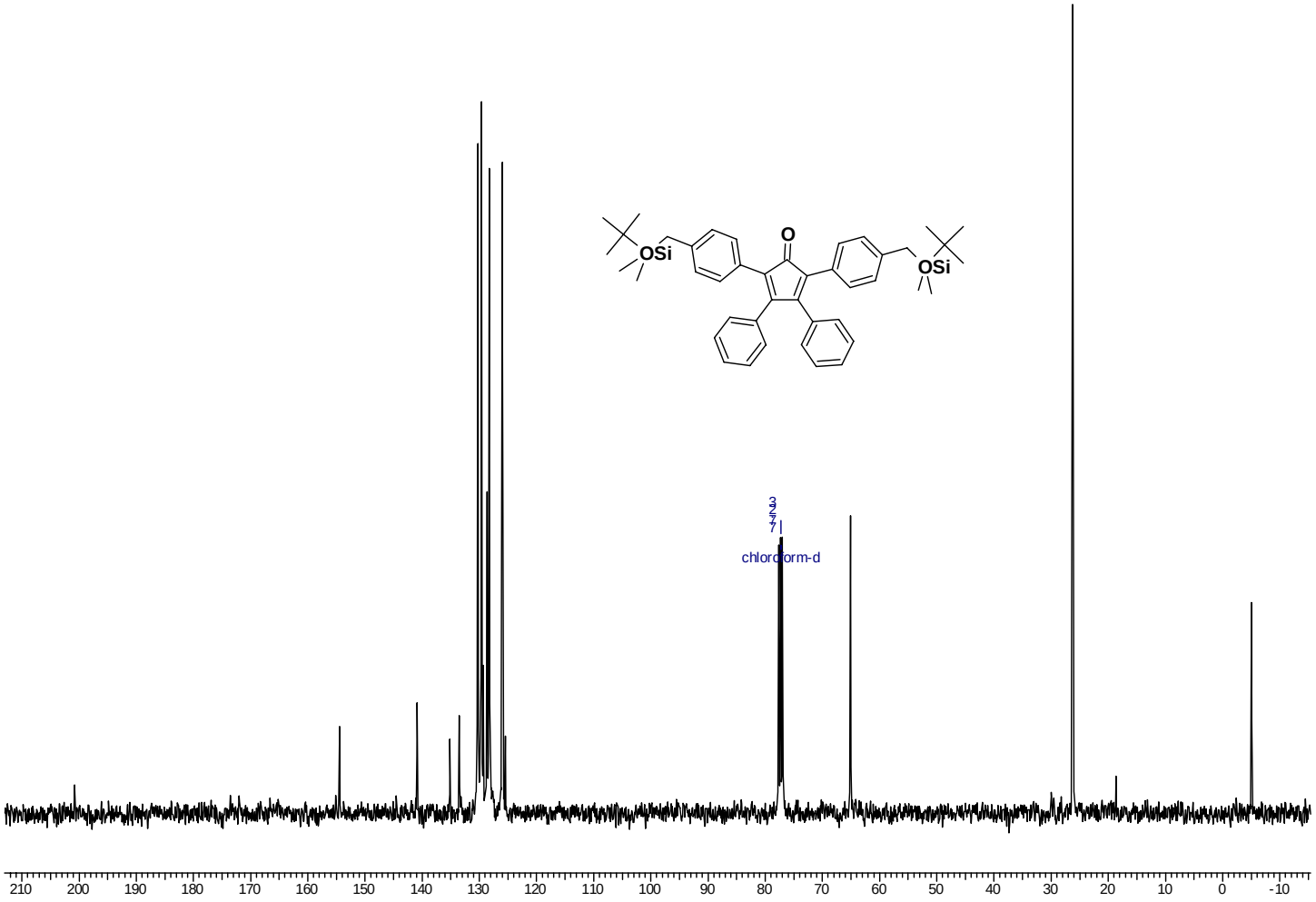
Acquisition Time (sec)	2.6214	***Comment***	13C OBSERVE			***Date***	Oct 17 2007	
Frequency (MHz)	50.29	***Nucleus***	13C	***Number of Transients***	1000	***Original Points Count***	18720	***Points Count***	32768
Solvent	CDCl3	***Sweep Width (Hz)***	12500.00			***Temperature (grad C)***	29.000		



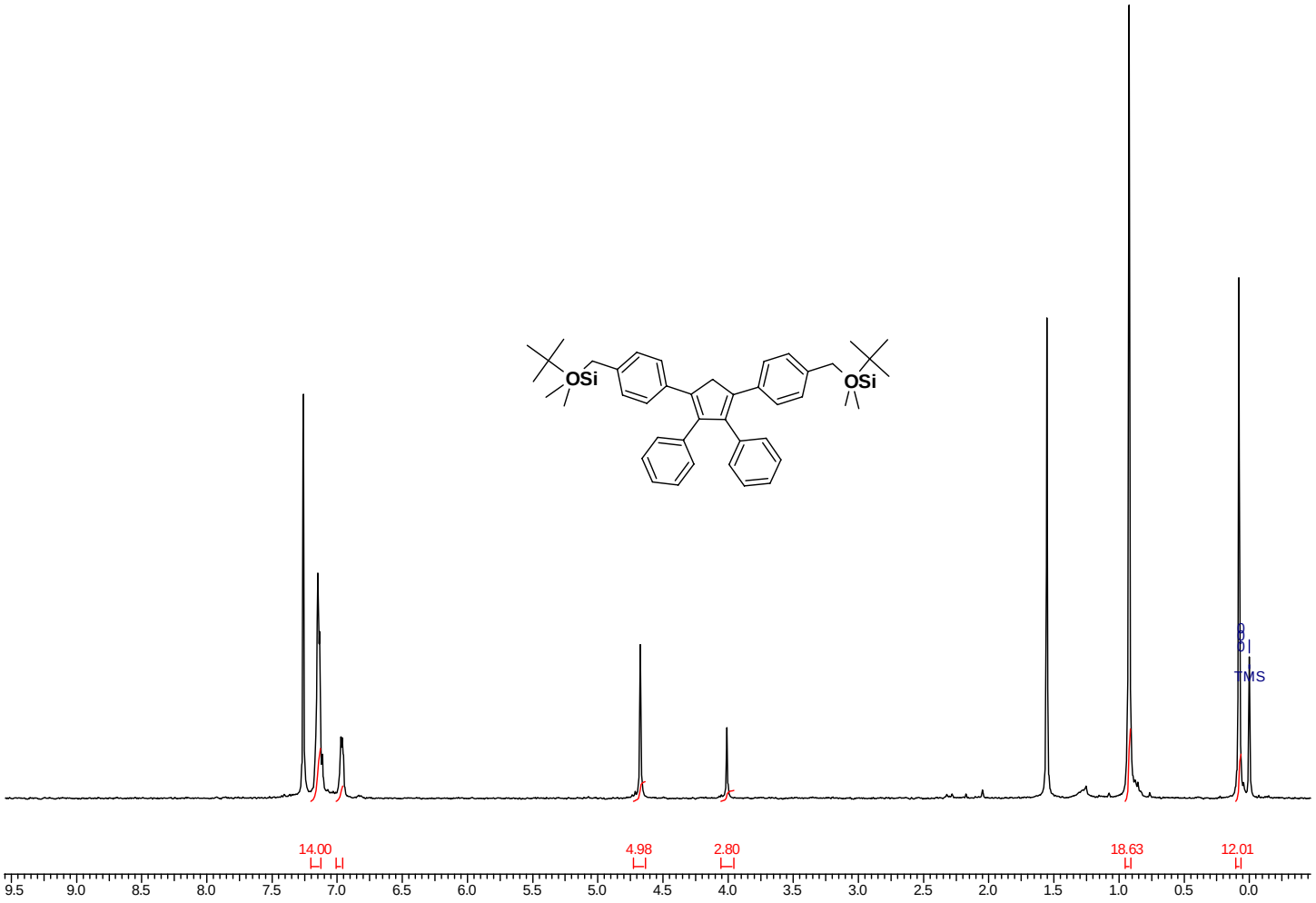
Acquisition Time (sec)	5.4608	***Comment***	STANDARD 1H OBSERVE			***Date***	May 3 2005
Frequency (MHz)	399.79	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	22208	***Points Count***	32768
Solvent	CDCl3	***Sweep Width (Hz)***	6000.60	***Temperature (grad C)***	29.000				



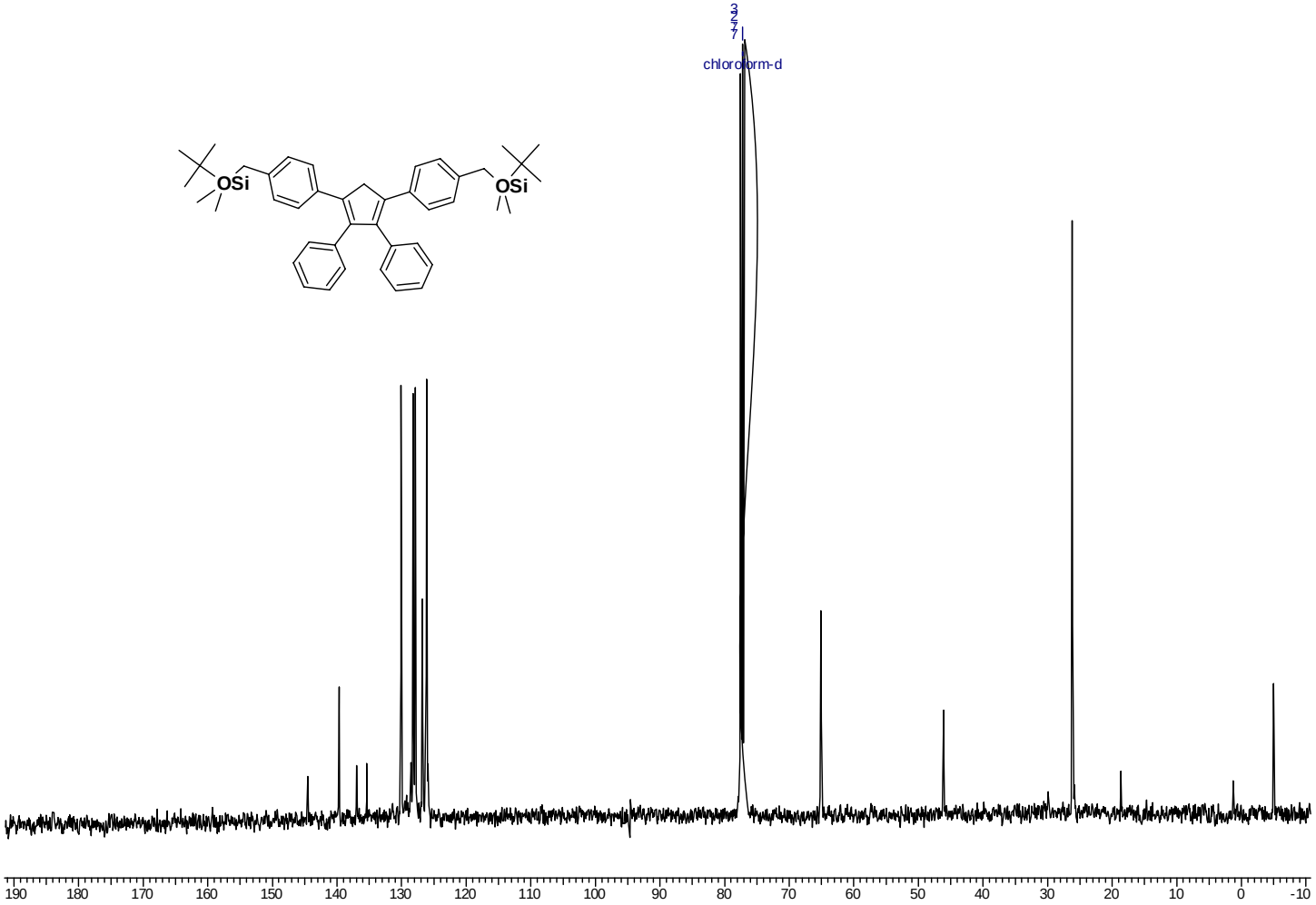
Acquisition Time (sec)	1.3107	***Comment***	13C OBSERVE		***Date***	Jul 26 2006	
Frequency (MHz)	100.53	***Nucleus***	13C	***Number of Transients*** 1000	***Original Points Count***	29984	***Points Count*** 32768
Solvent	CDCl3	***Sweep Width (Hz)***	25000.00		***Temperature (grad C)***	29.000	



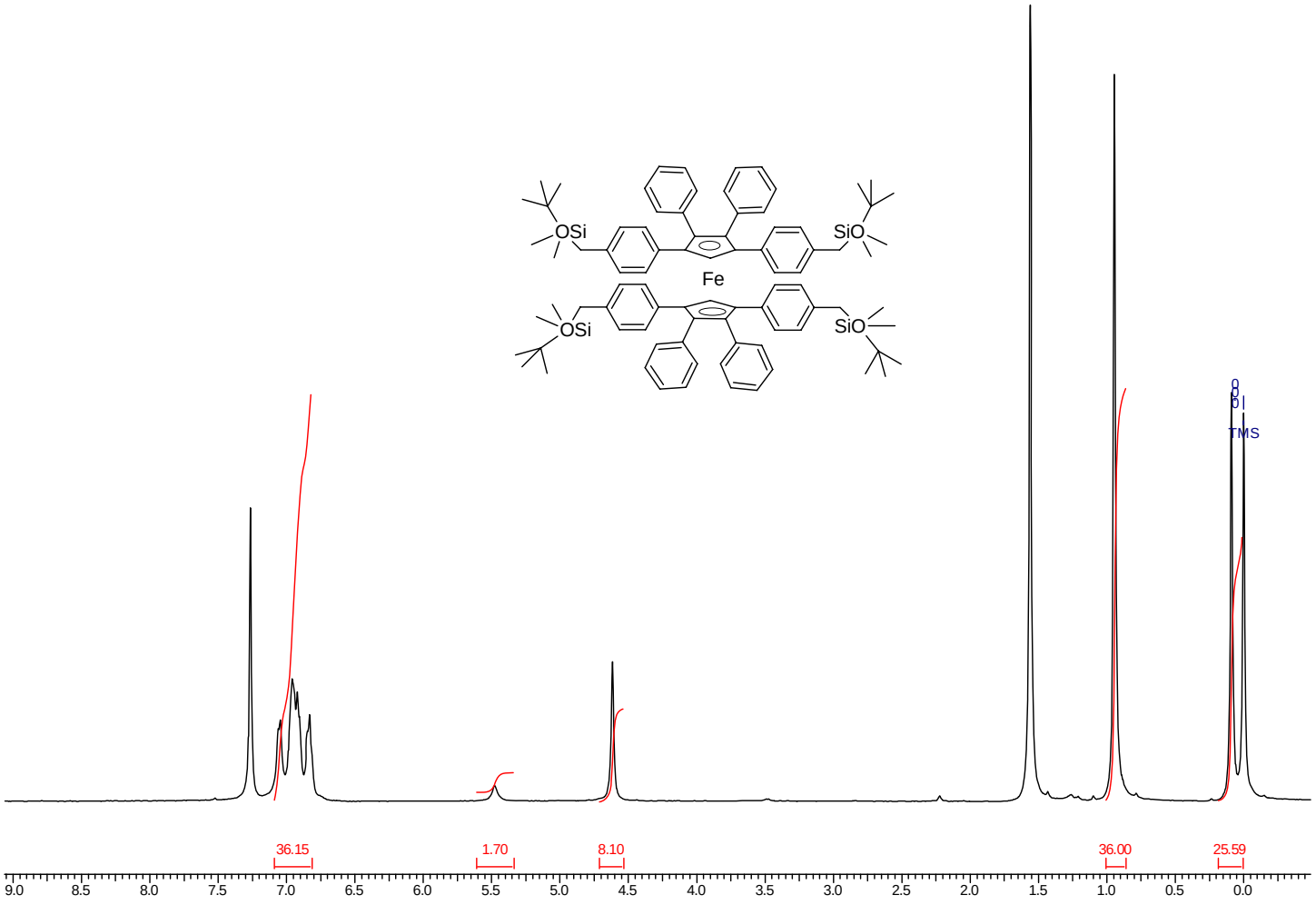
Acquisition Time (sec)	5.4608	***Comment***	STANDARD 1H OBSERVE			***Date***	Nov 28 2005
Frequency (MHz)	399.79	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	22208
Solvent	CDCl3	***Sweep Width (Hz)***	6000.60	***Temperature (grad C)***	29.000		



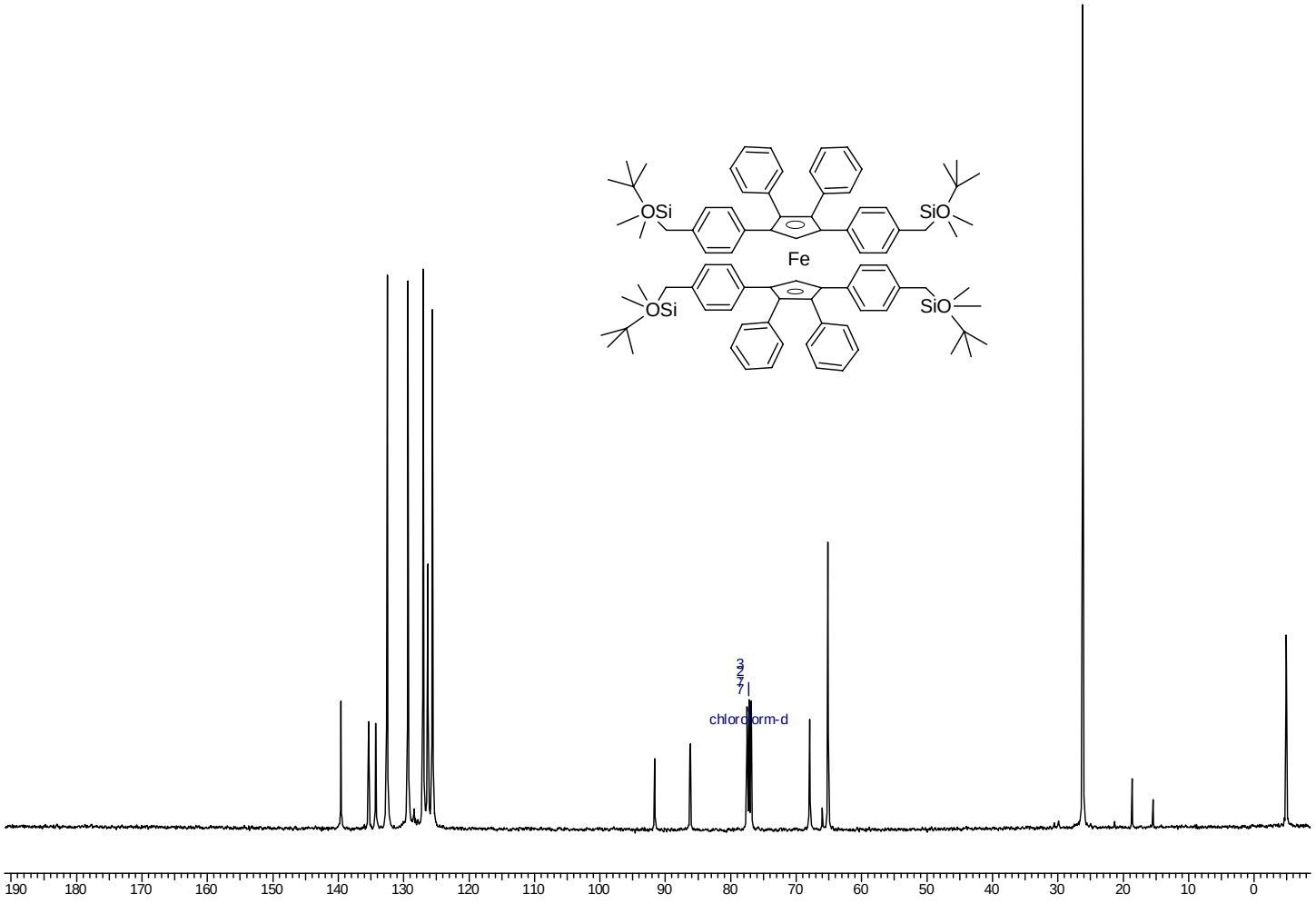
Acquisition Time (sec)	1.3107	***Comment***	13C OBSERVE		***Date***	Aug 2 2005	
Frequency (MHz)	100.54	***Nucleus***	13C	***Number of Transients*** 24000	***Original Points Count***	29984	***Points Count*** 32768
Solvent	CDCl3	***Sweep Width (Hz)***	25000.00		***Temperature (grad C)***	29.000	



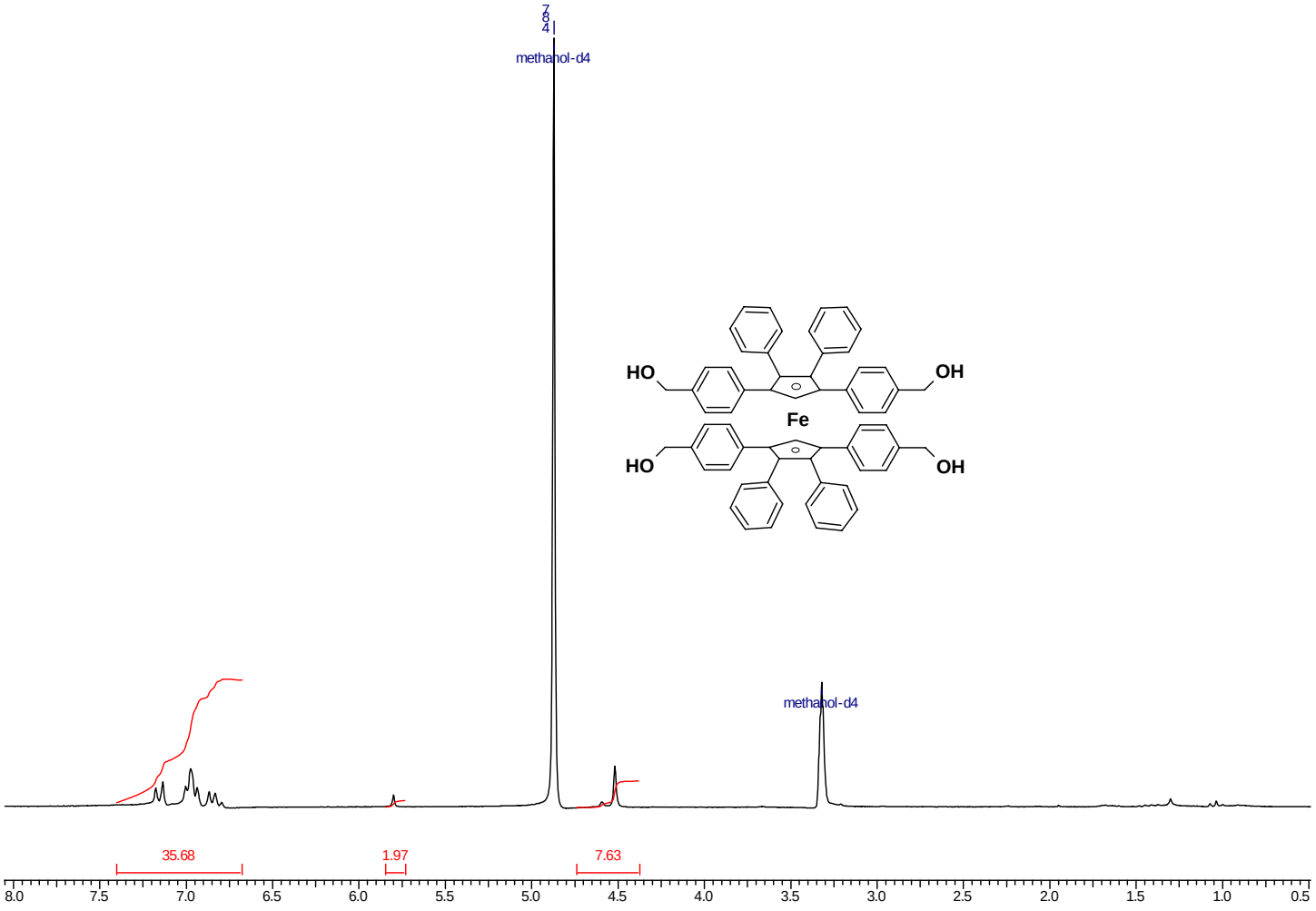
Acquisition Time (sec)	6.5536	***Comment***	STANDARD 1H OBSERVE			***Date***	Jul 13 2005
Frequency (MHz)	399.79	***Nucleus***	1H	***Number of Transients***	32	***Original Points Count***	18505
Solvent	CDCl3	***Sweep Width (Hz)***	5000.00	***Temperature (grad C)***	29.000		



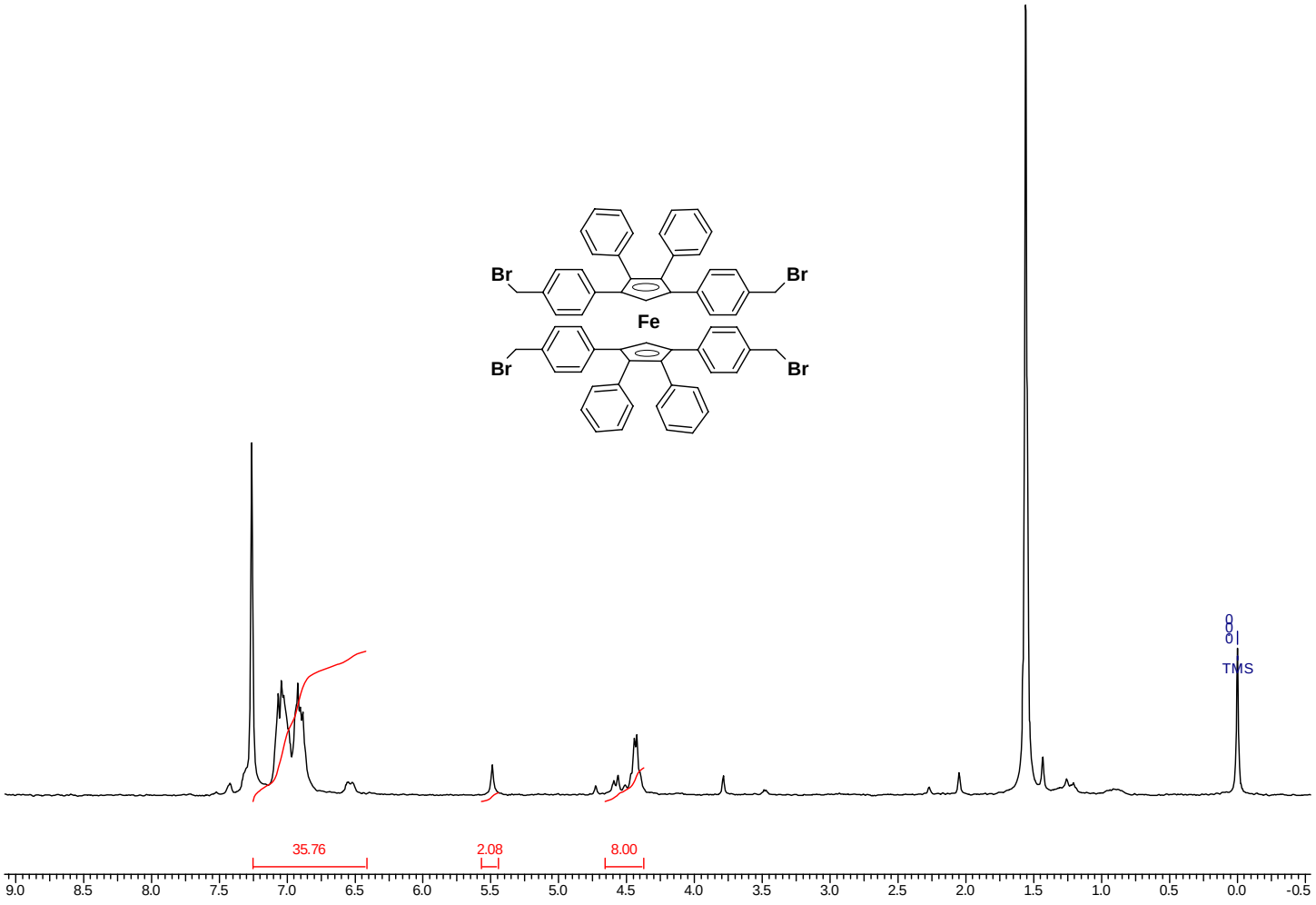
Acquisition Time (sec)	1.3107	***Comment***	13C OBSERVE			***Date***	Jul 29 2005	
Frequency (MHz)	100.54	***Nucleus***	13C	***Original Points Count***	29984	***Points Count***	32768	***Solvent***	CDCl3
Sweep Width (Hz)	25000.00			***Temperature (grad C)***	29.000				



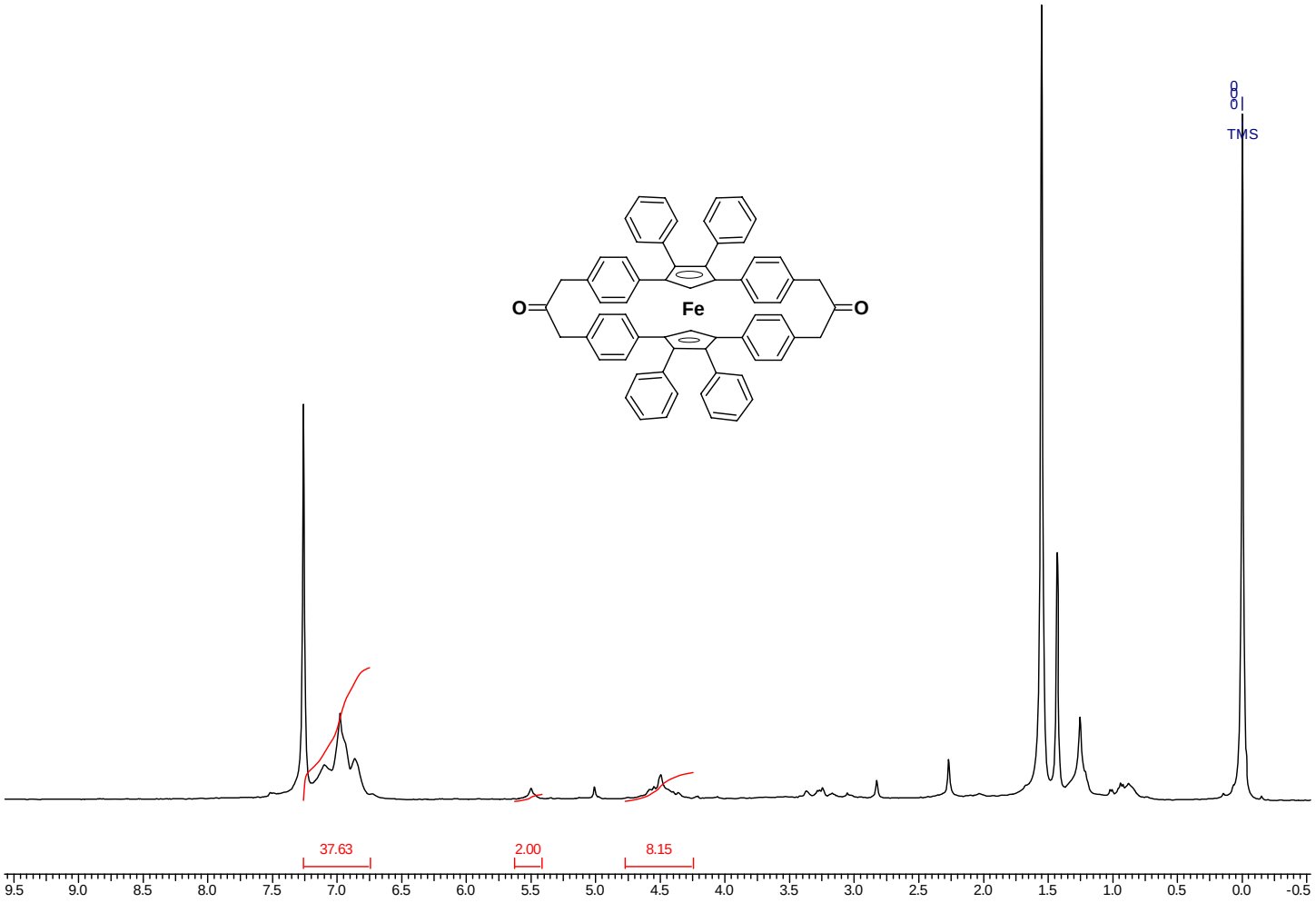
Acquisition Time (sec)	2.7304	***Comment***	STANDARD 1H OBSERVE			***Date***	Aug 14 2006
Frequency (MHz)	199.98	***Nucleus***	1H	***Number of Transients***	200	***Original Points Count***	5984
Solvent	CD3OD	***Sweep Width (Hz)***	3000.30	***Temperature (grad C)***	29.000		



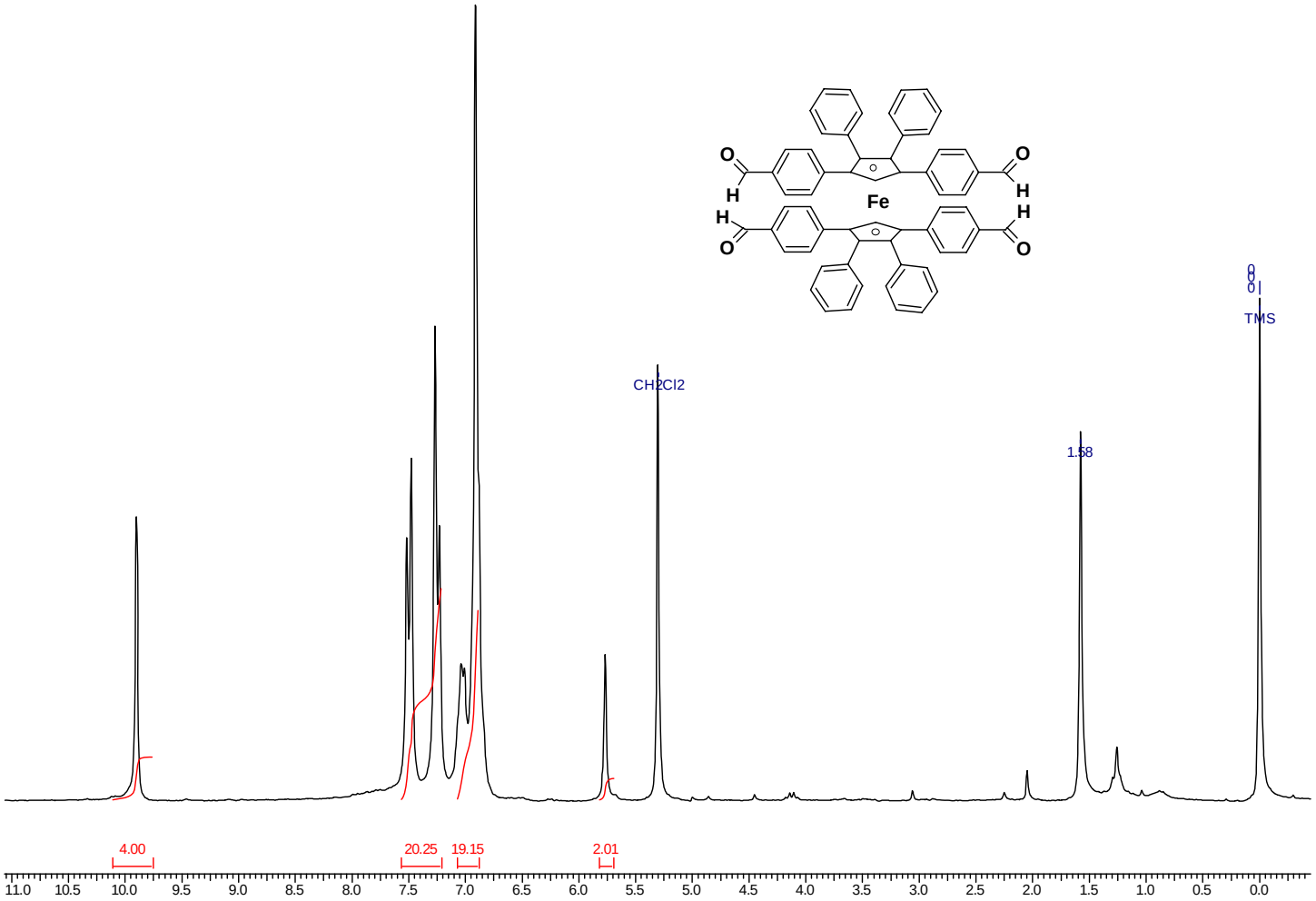
Acquisition Time (sec)	6.5536	***Comment***	STANDARD 1H OBSERVE			***Date***	Jul 31 2005	
Frequency (MHz)	399.79	***Nucleus***	1H	***Number of Transients***	64	***Original Points Count***	18505	***Points Count*** 32768
Solvent	CDCl3	***Sweep Width (Hz)***	5000.00	***Temperature (grad C)***	29.000			



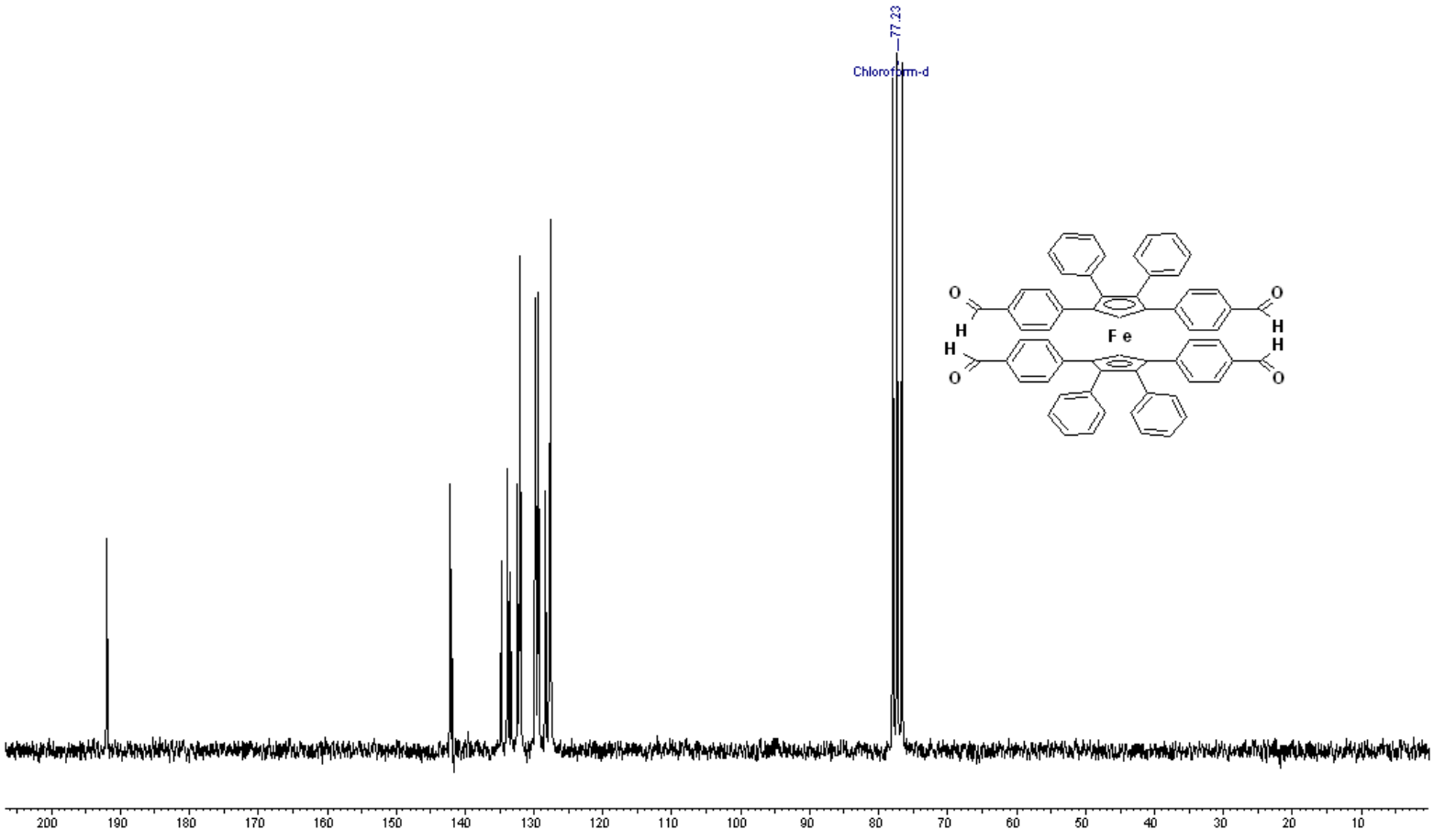
Acquisition Time (sec)	5.4608	***Comment***	STANDARD 1H OBSERVE			***Date***	Sep 15 2005
Frequency (MHz)	399.79	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	22208
Solvent	CDCl3	***Sweep Width (Hz)***	6000.60	***Temperature (grad C)***	29.000		



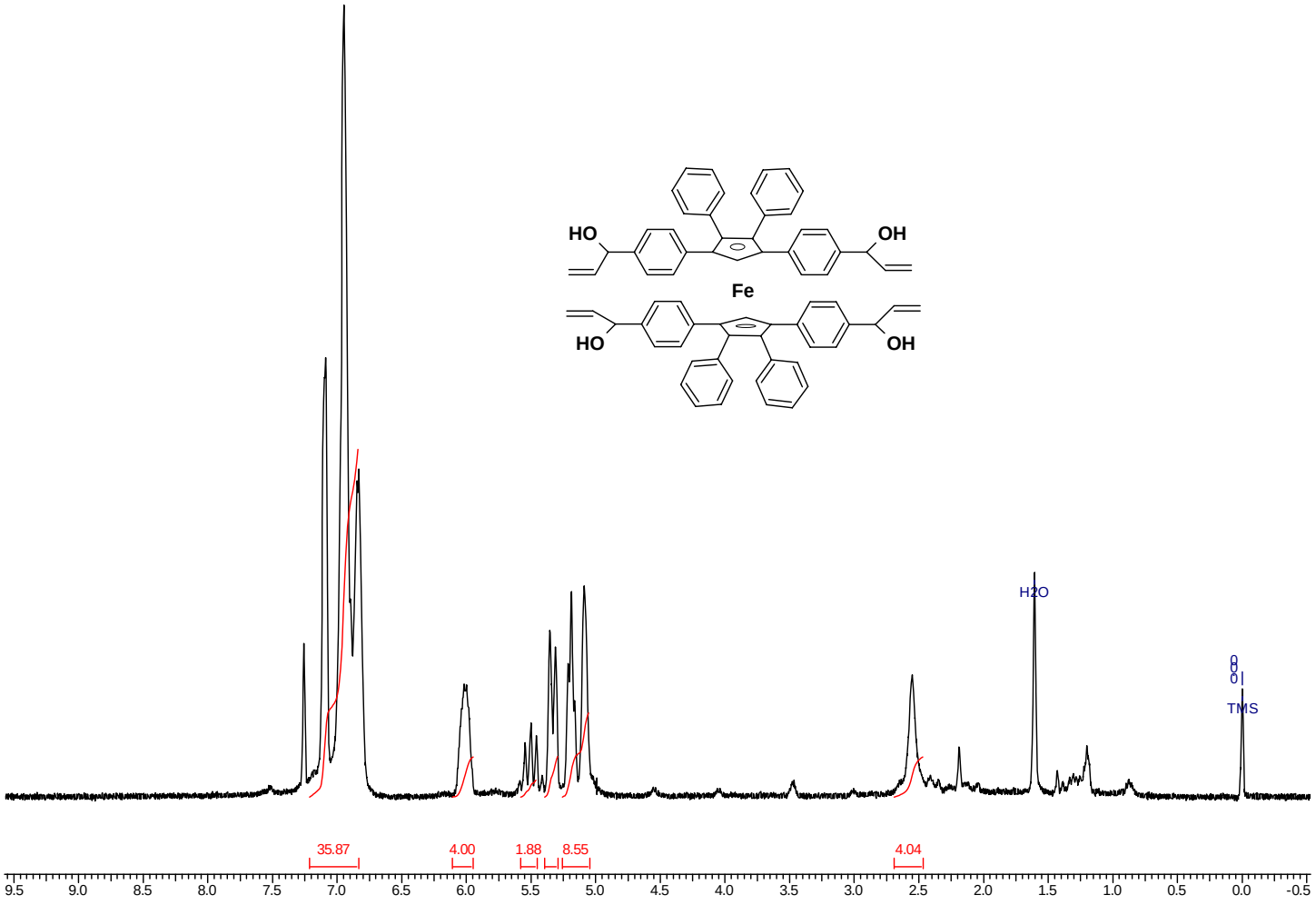
Acquisition Time (sec)	2.7304	***Comment***	STANDARD 1H OBSERVE			***Date***	Jun 26 2006
Frequency (MHz)	199.98	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	5984	***Points Count***	8192
Solvent	CDCl3	***Sweep Width (Hz)***	3000.30	***Temperature (grad C)***	29.000				



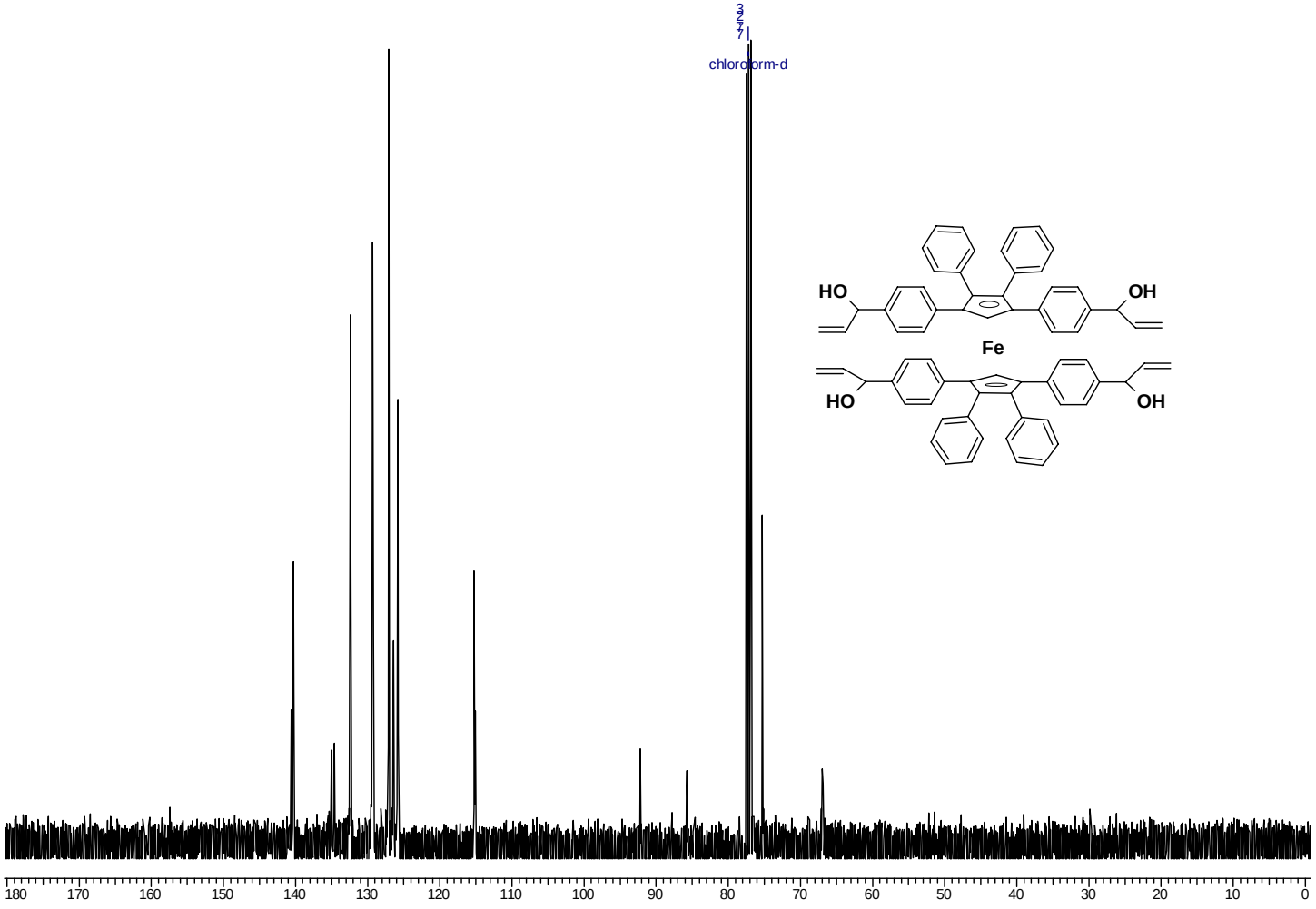
Acquisition Time (sec)	2.6214	Comment	13C OBSERVE			Date	Nov 24 2008
Frequency (MHz)	50.29	Nucleus	13C	Number of Transients	10000	Original Points Count	18720	Points Count	32768
Solvent	CDCl3	Sweep Width (Hz)	12500.00			Temperature (grad C)	29.000		



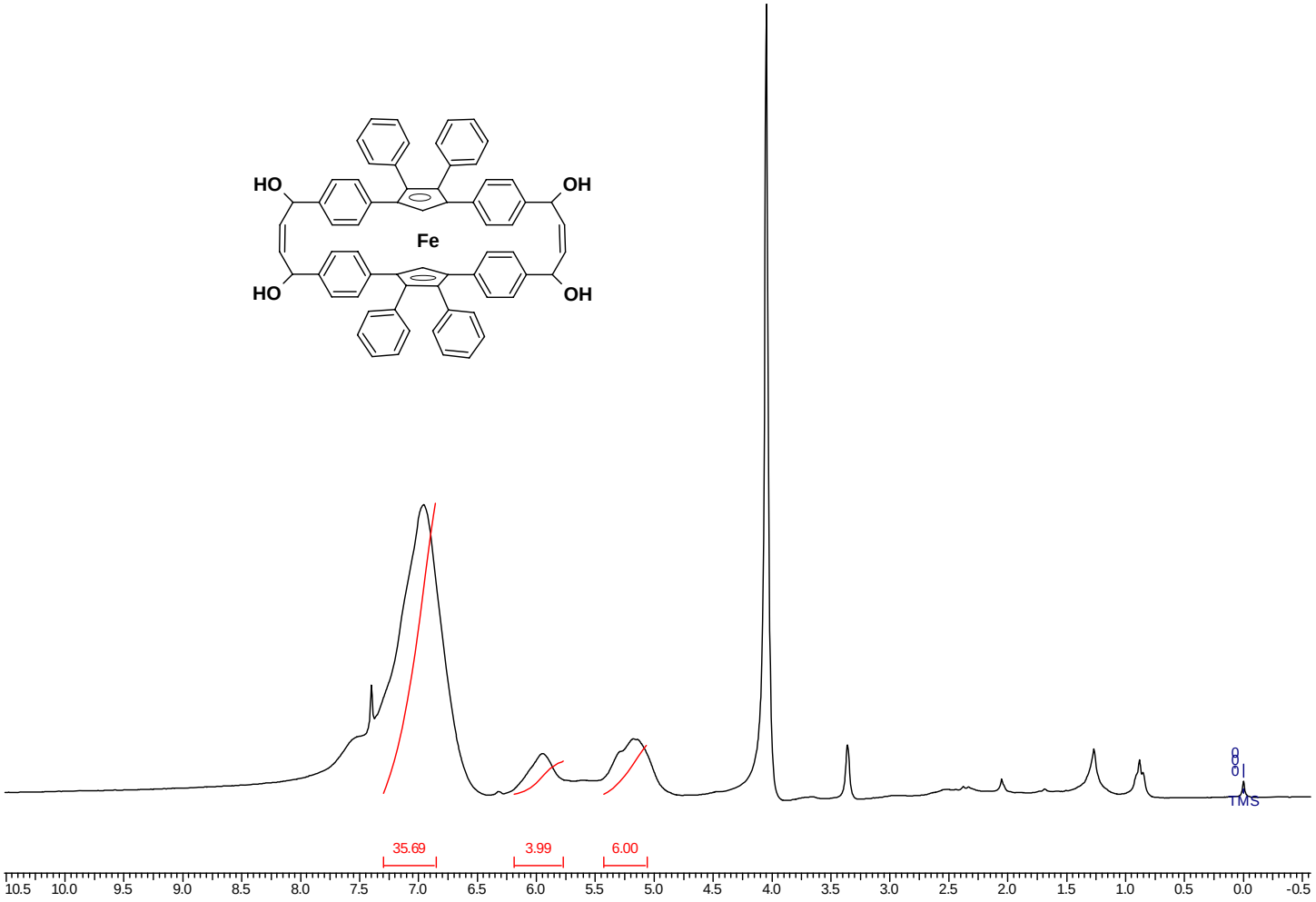
Acquisition Time (sec)	5.4608	***Comment***	STANDARD 1H OBSERVE			***Date***	Jul 26 2006
Frequency (MHz)	399.78	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	22208
Solvent	CDCl3	***Sweep Width (Hz)***	6000.60	***Temperature (grad C)***	29.000		



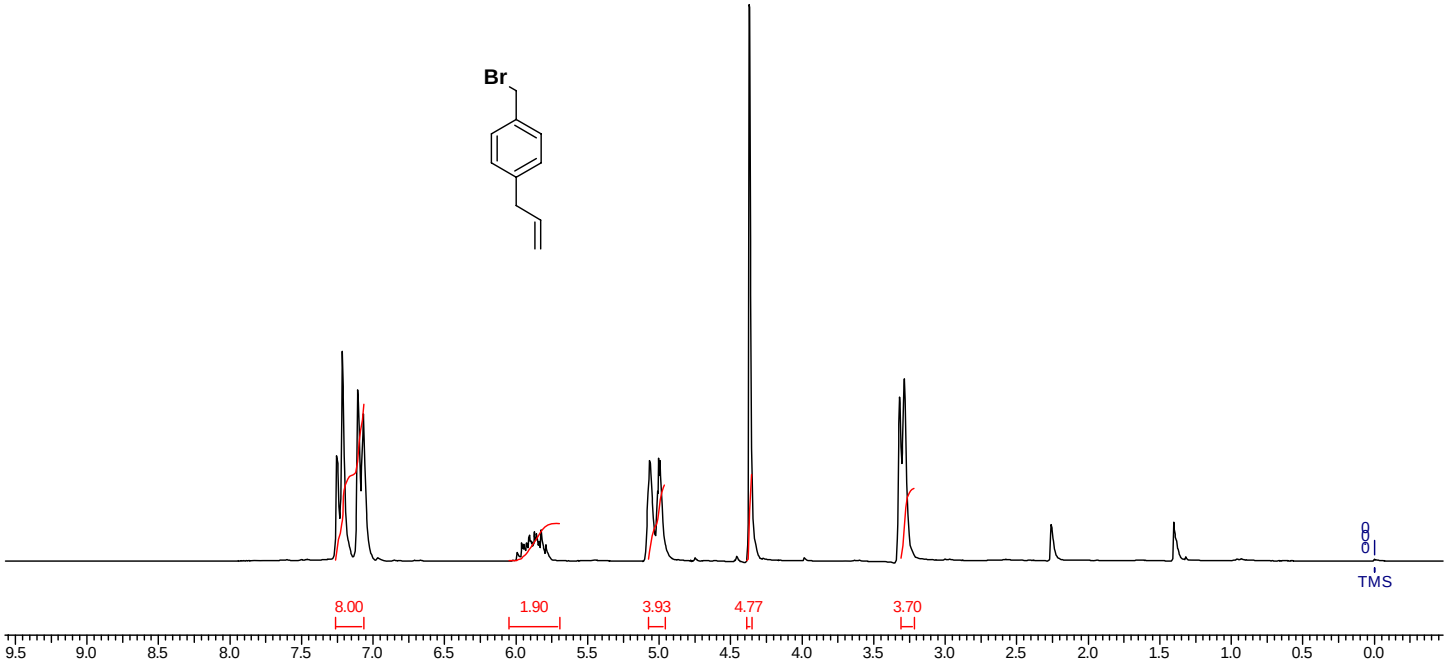
Acquisition Time (sec)	1.3107	***Comment***	13C OBSERVE		***Date***	Jul 26 2006	
Frequency (MHz)	100.53	***Nucleus***	13C	***Number of Transients*** 25000	***Original Points Count***	29984	***Points Count*** 32768
Solvent	CDCl3	***Sweep Width (Hz)***	25000.00		***Temperature (grad C)***	29.000	



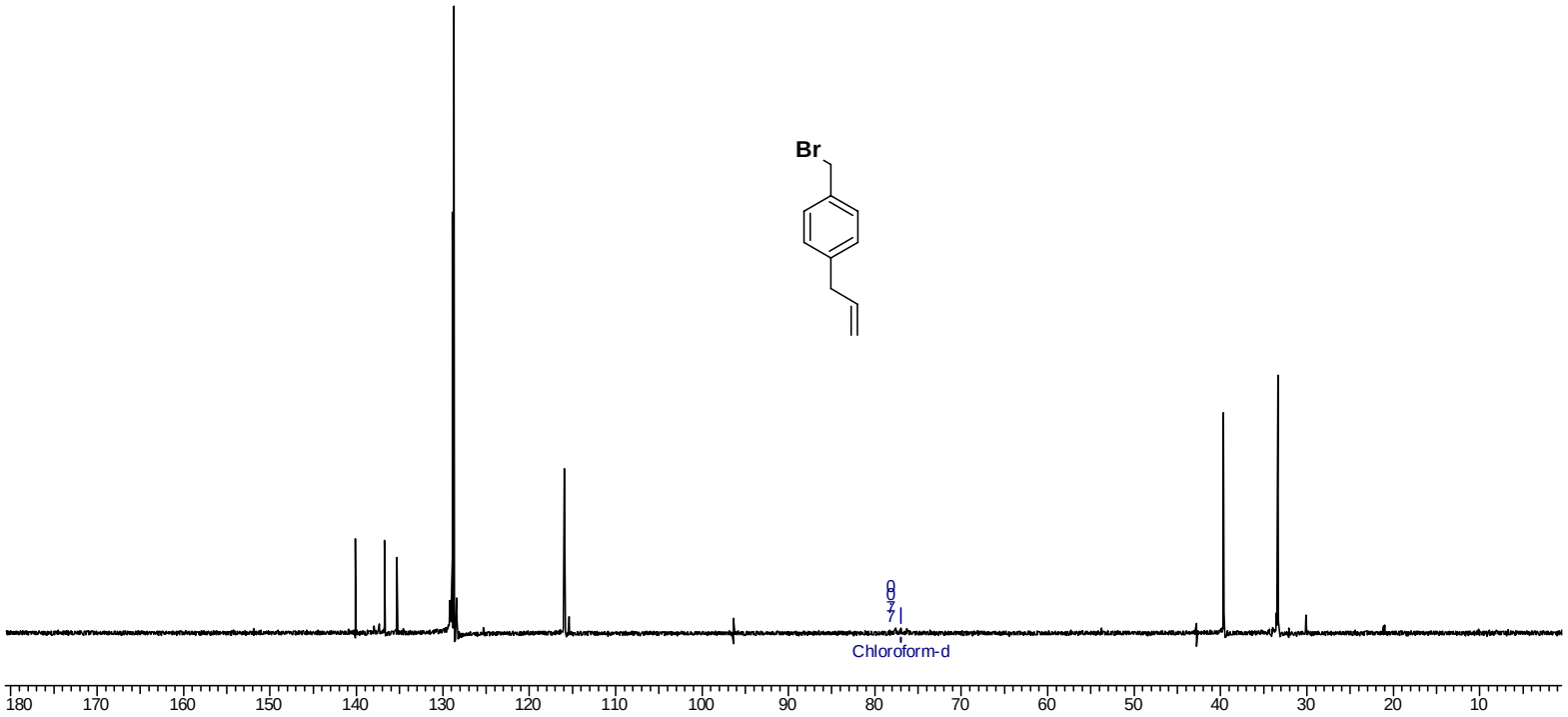
Acquisition Time (sec)	2.7304	***Comment***	STANDARD 1H OBSERVE			***Date***	Aug 9 2006
Frequency (MHz)	199.98	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	5984
Solvent	CDCl3	***Sweep Width (Hz)***	3000.30	***Temperature (grad C)***	29.000		



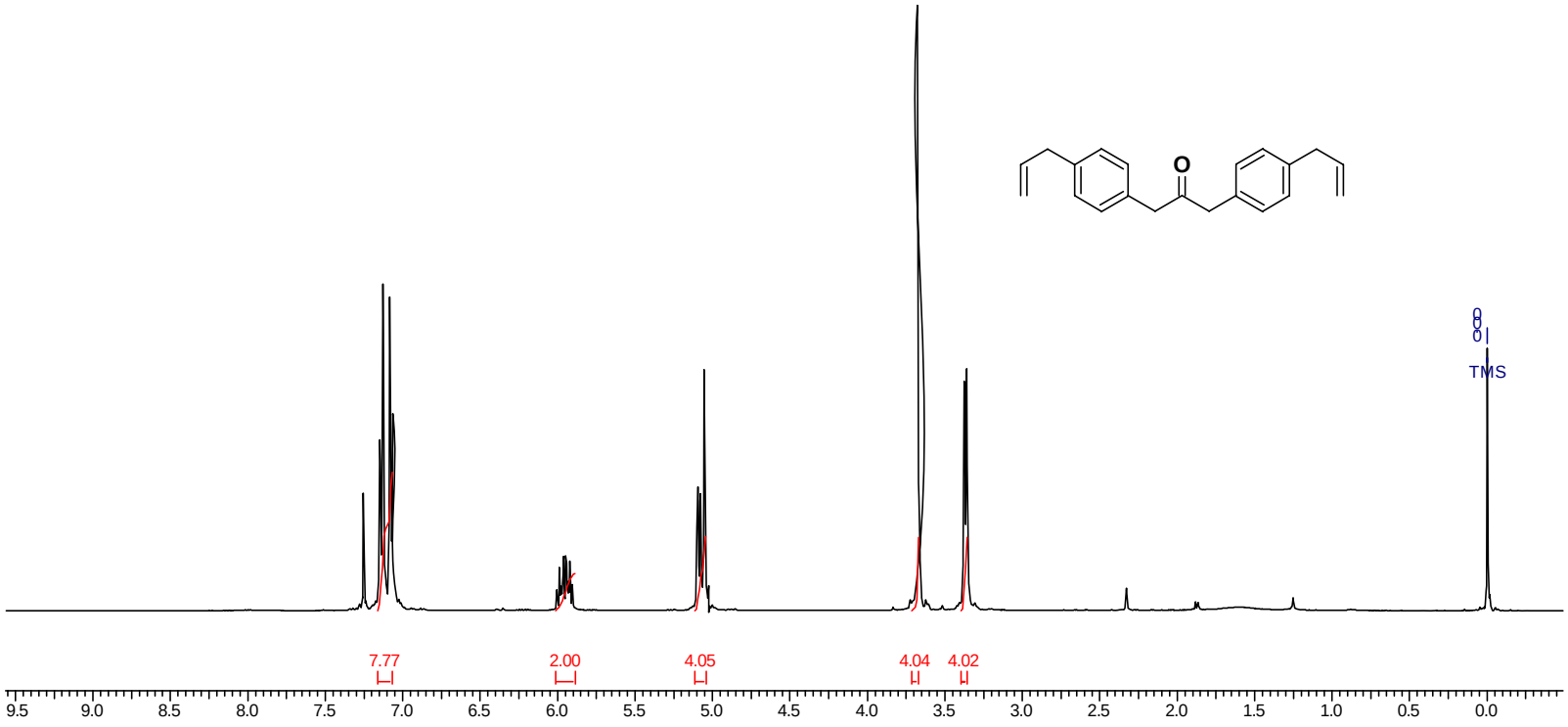
Acquisition Time (sec)	2.7304	***Comment***	STANDARD 1H OBSERVE			***Date***	May 23 2007
Frequency (MHz)	199.98	***Nucleus***	1H	***Number of Transients***	64	***Original Points Count***	5984	***Points Count***	8192
Solvent	CDCl3	***Sweep Width (Hz)***	3000.30	***Temperature (grad C)***	29.000				



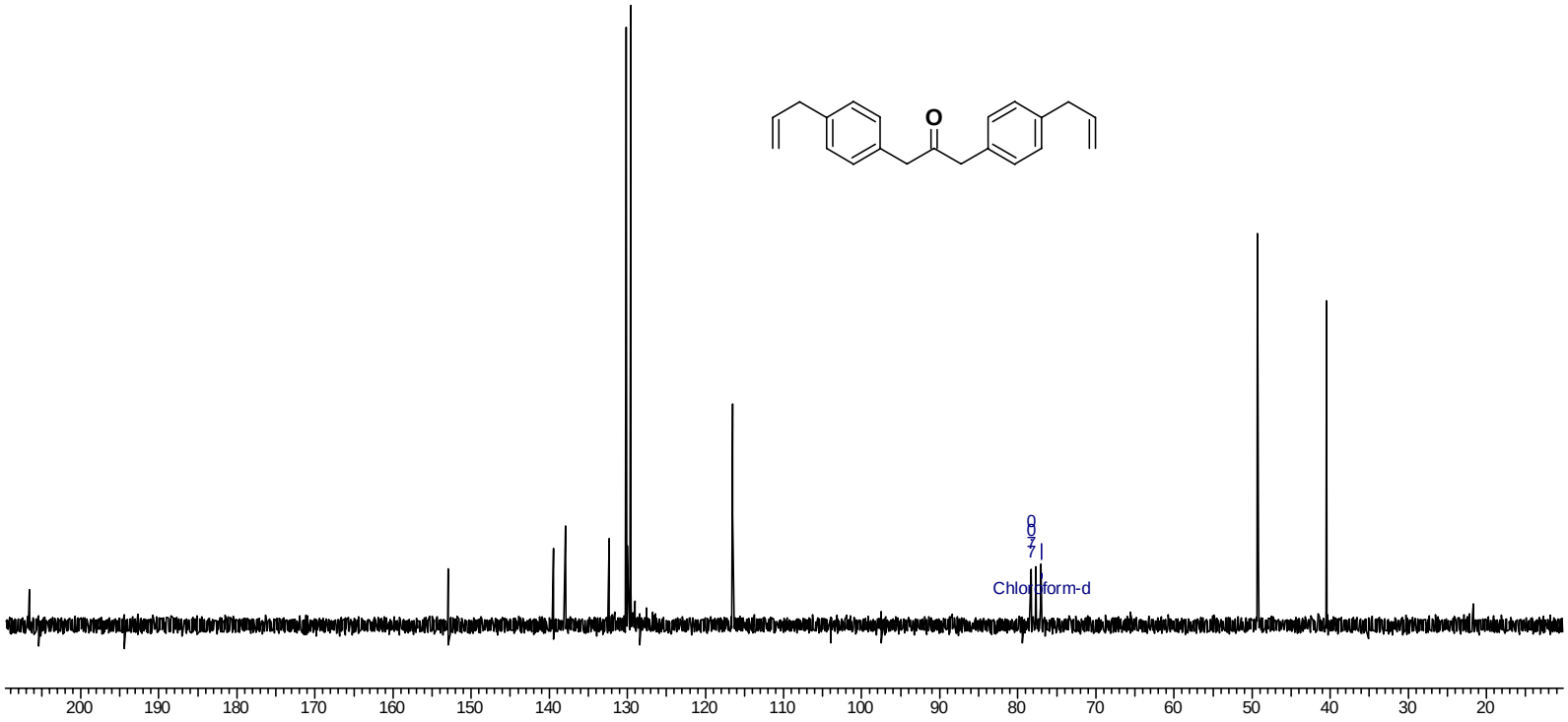
Acquisition Time (sec)	2.6214	***Comment***	13C OBSERVE		***Date***	May 23 2007	
Frequency (MHz)	50.29	***Nucleus***	13C	***Number of Transients*** 500	***Original Points Count***	18720	***Points Count*** 32768
Solvent	CDCl3	***Sweep Width (Hz)***	12500.00		***Temperature (grad C)***	29.000	

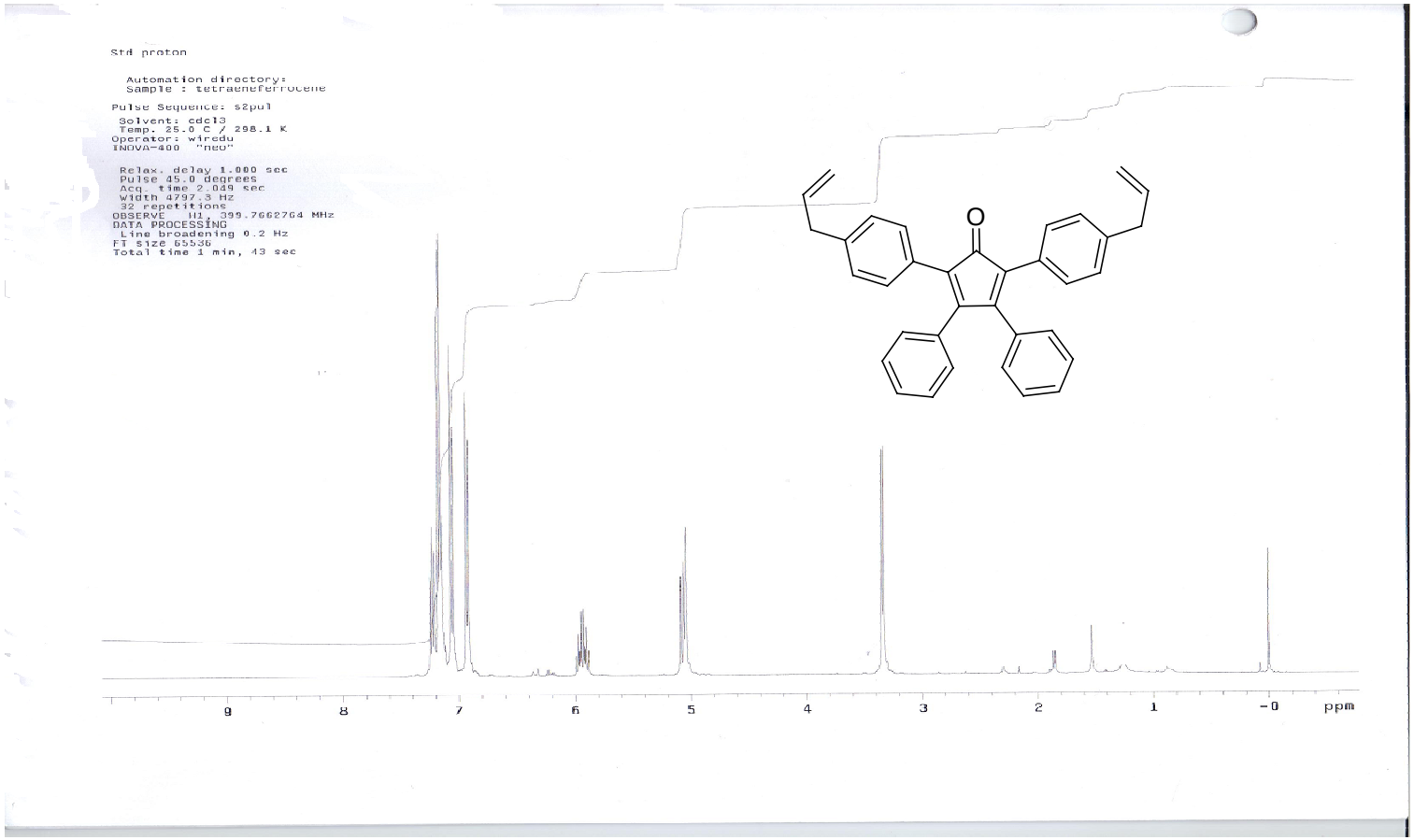


Acquisition Time (sec)	3.4154	***Comment***	Std proton		***Date***	Sep 9 2008	
Frequency (MHz)	399.76	***Nucleus***	1H	***Number of Transients*** 100	***Original Points Count***	9827	***Points Count*** 16384
Solvent	CDCl3	***Sweep Width (Hz)***	4797.03		***Temperature (grad C)***	25.000	

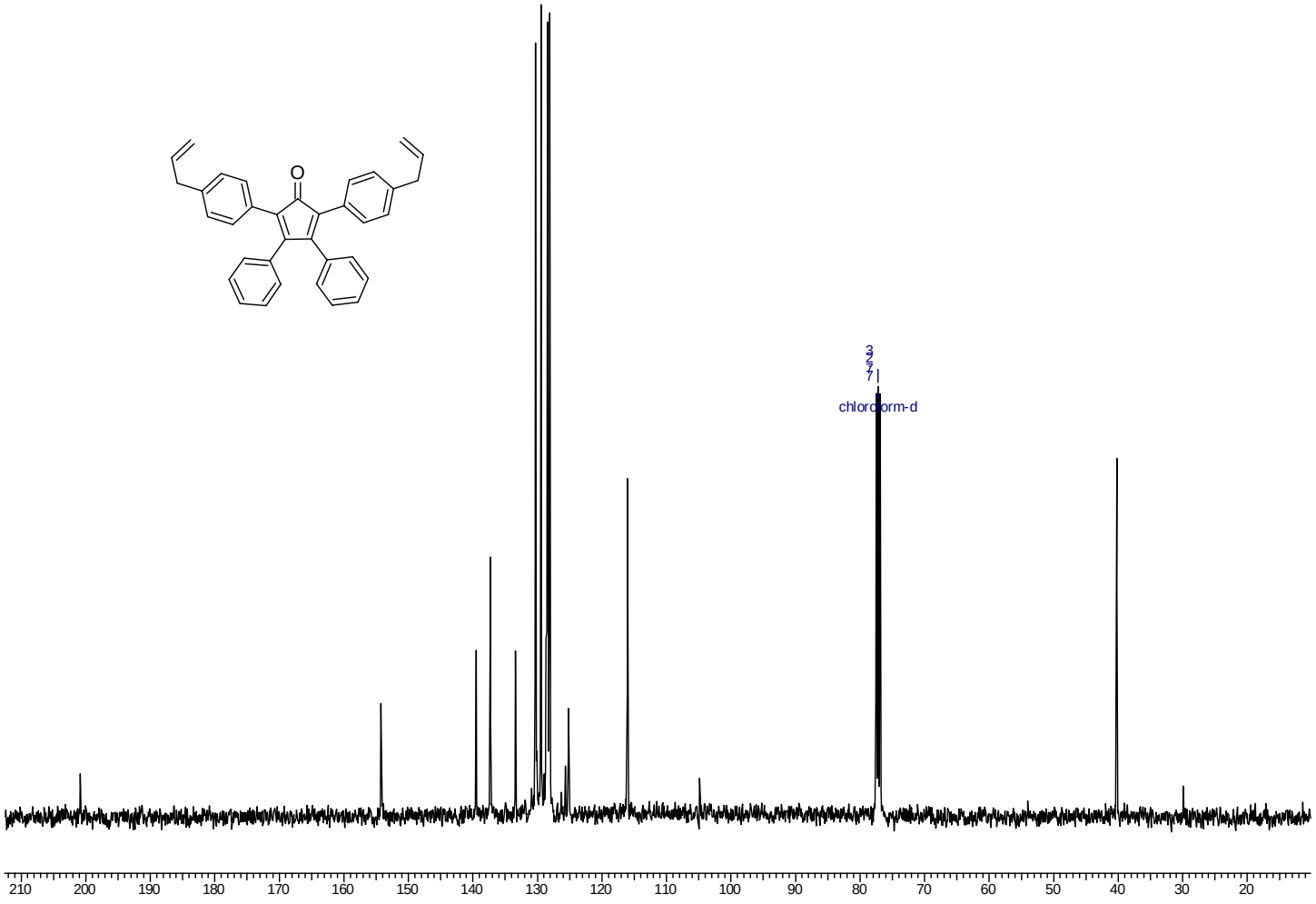


Acquisition Time (sec)	2.6214	***Comment***	13C OBSERVE			***Date***	Jul 26 2007		
Frequency (MHz)	50.29	***Nucleus***	13C	***Number of Transients***	1024	***Original Points Count***	18720	***Points Count***	32768
Solvent	CDCl3	***Sweep Width (Hz)***	12500.00			***Temperature (grad C)***	29.000		

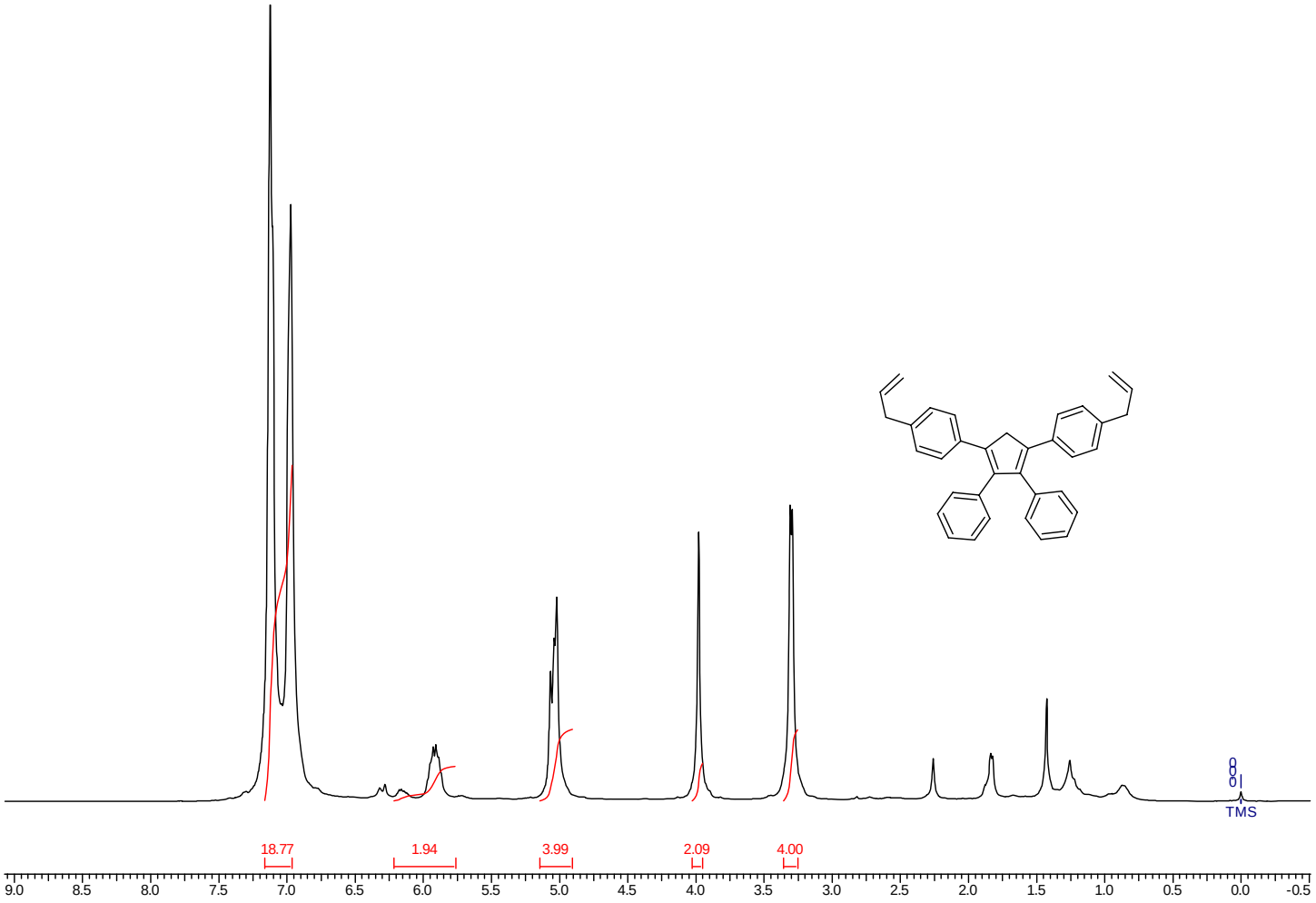



Std proton
Automation directory:
Sample : tetraeneferrocene
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: wiredu
INOVA-400 "neo"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 4797.3 Hz
32 repetitions
OBSERVE H1, 399.7662764 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 43 sec
O
9
8
7
6
5
4
3
2
1
-0
ppm

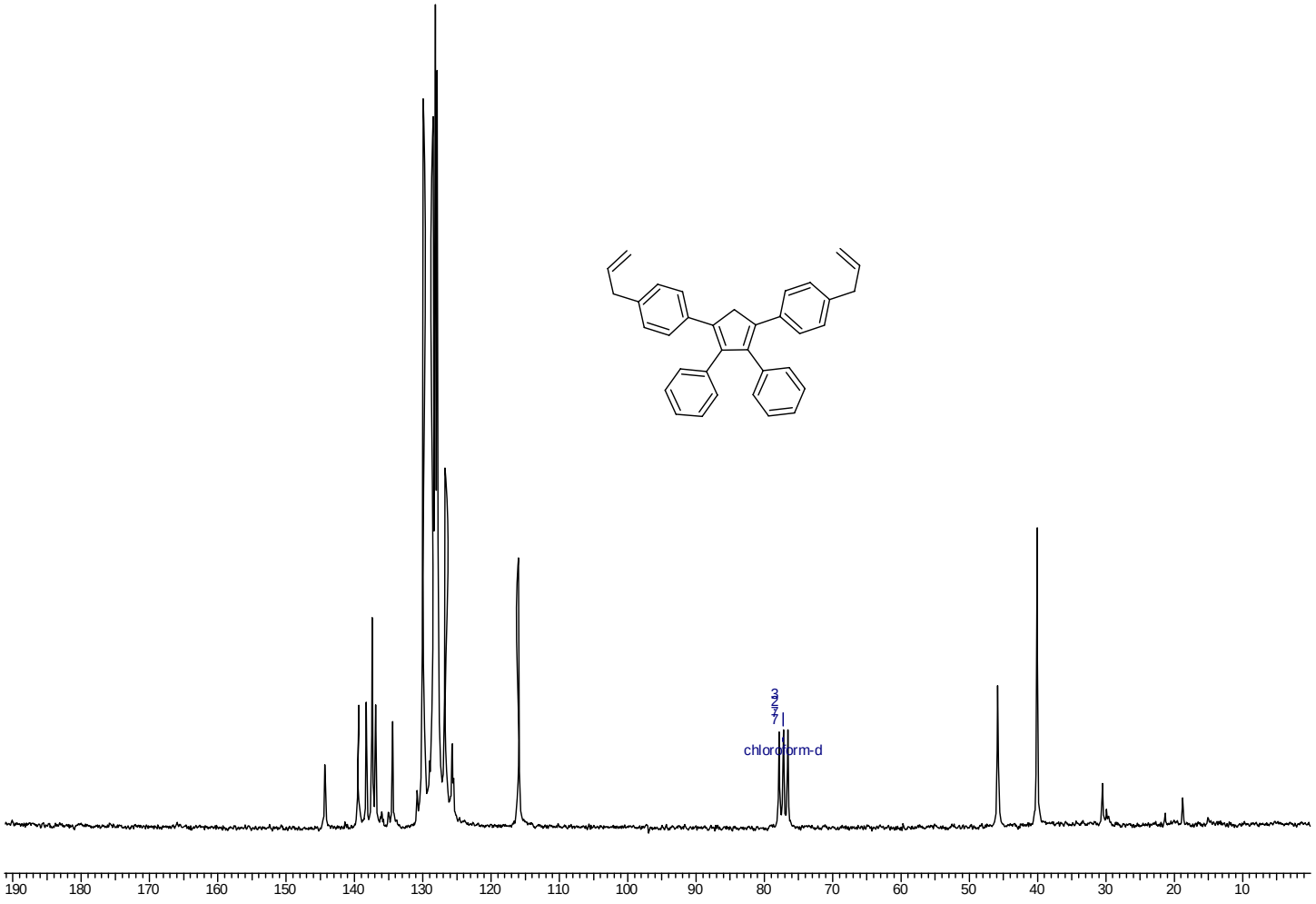
Acquisition Time (sec)	1.3582	***Comment***	Std proton			***Date***	Sep 8 2007		
Frequency (MHz)	100.53	***Nucleus***	13C	***Number of Transients***	14888	***Original Points Count***	31375	***Points Count***	32768
Solvent	CDCl3	***Sweep Width (Hz)***	24125.45			***Temperature (grad C)***	25.000		



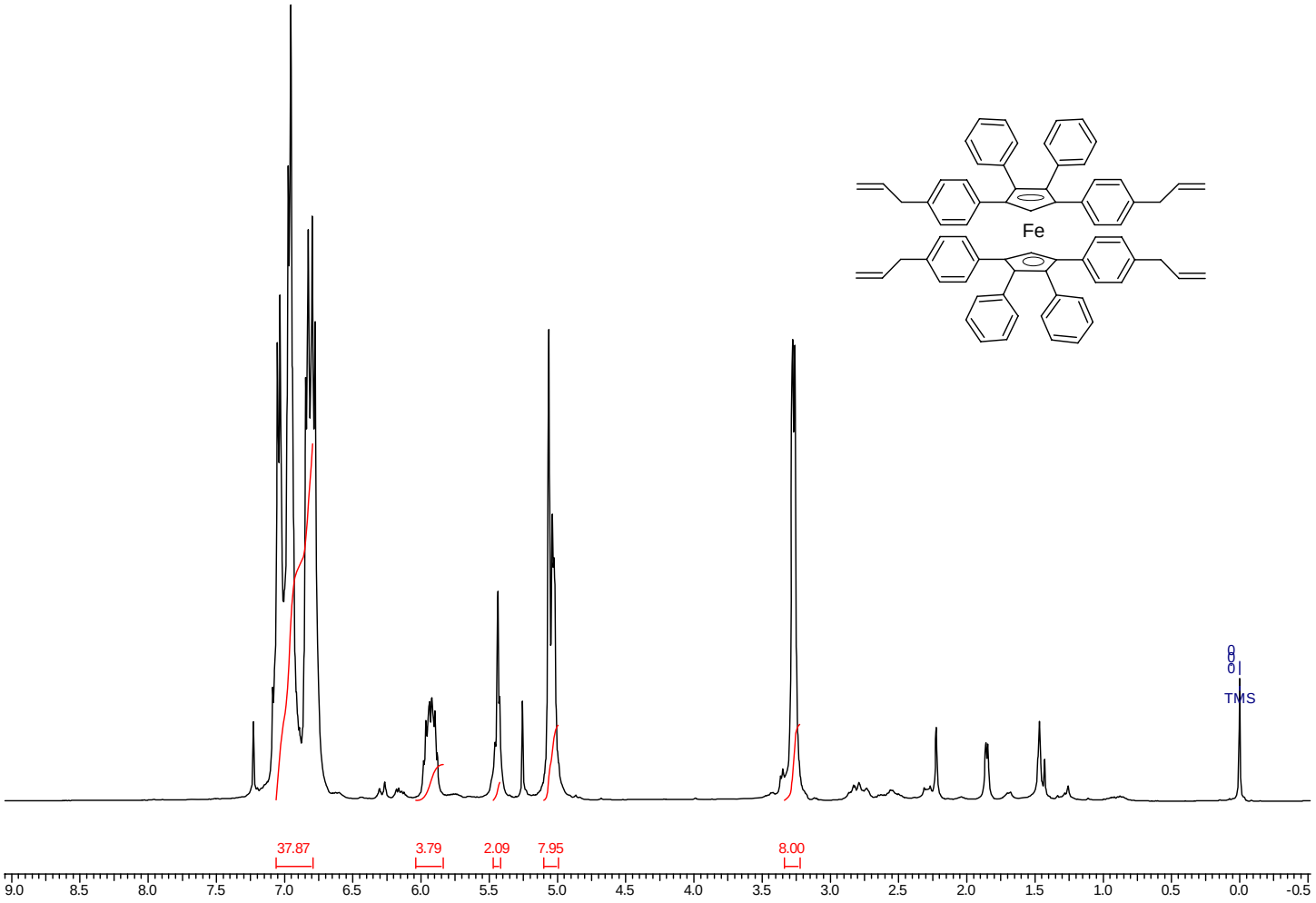
Acquisition Time (sec)	3.4154	***Comment***	Std proton			***Date***	Nov 21 2008	
Frequency (MHz)	399.76	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	9827	***Points Count*** 16384
Solvent	CDCl3	***Sweep Width (Hz)***	4797.03			***Temperature (grad C)***	25.000	



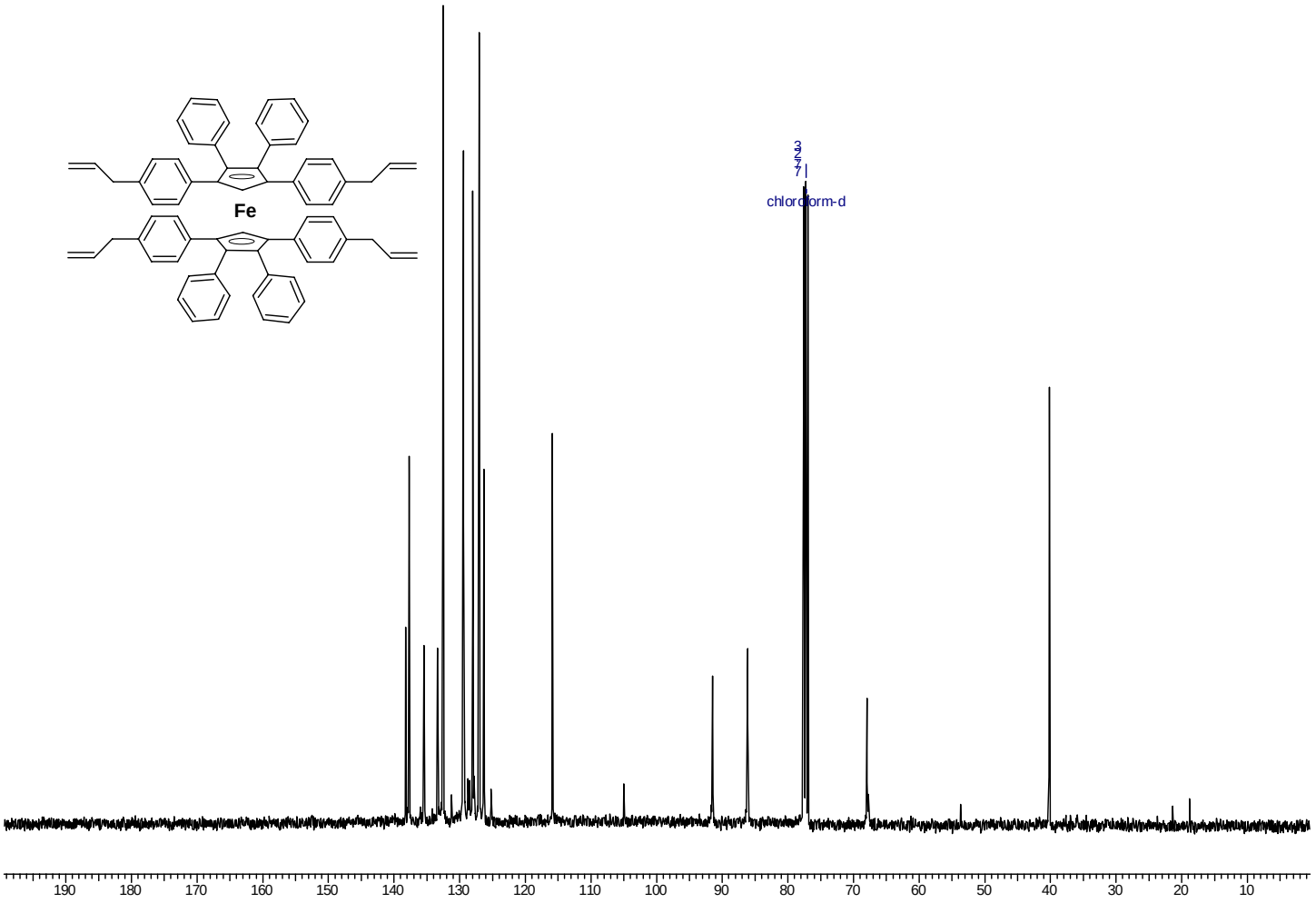
Acquisition Time (sec)	2.6214	***Comment***	13C OBSERVE		***Date***	Nov 19 2008	
Frequency (MHz)	50.29	***Nucleus***	13C	***Number of Transients*** 25000	***Original Points Count***	18720	***Points Count*** 32768
Solvent	CDCl3	***Sweep Width (Hz)***	12500.00		***Temperature (grad C)***	29.000	



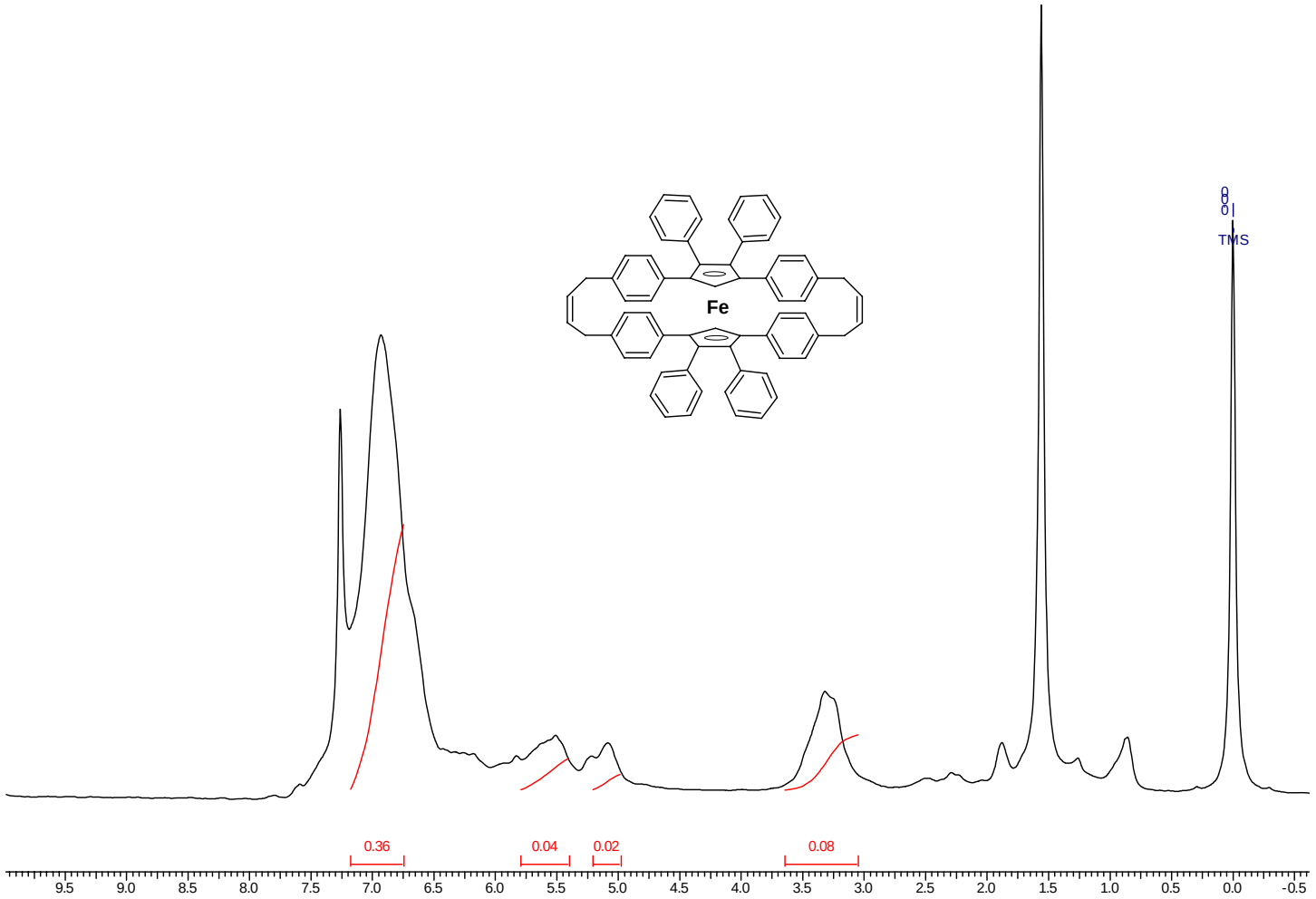
Acquisition Time (sec)	3.4152			***Comment***	Std proton			***Date***	Sep 18 2007
Frequency (MHz)	399.77			***Nucleus***	1H	***Number of Transients***	64	***Original Points Count***	9828	***Points Count***	16384
Solvent	cdcl3	***Sweep Width (Hz)***	4797.31			***Temperature (grad C)***	25.000		



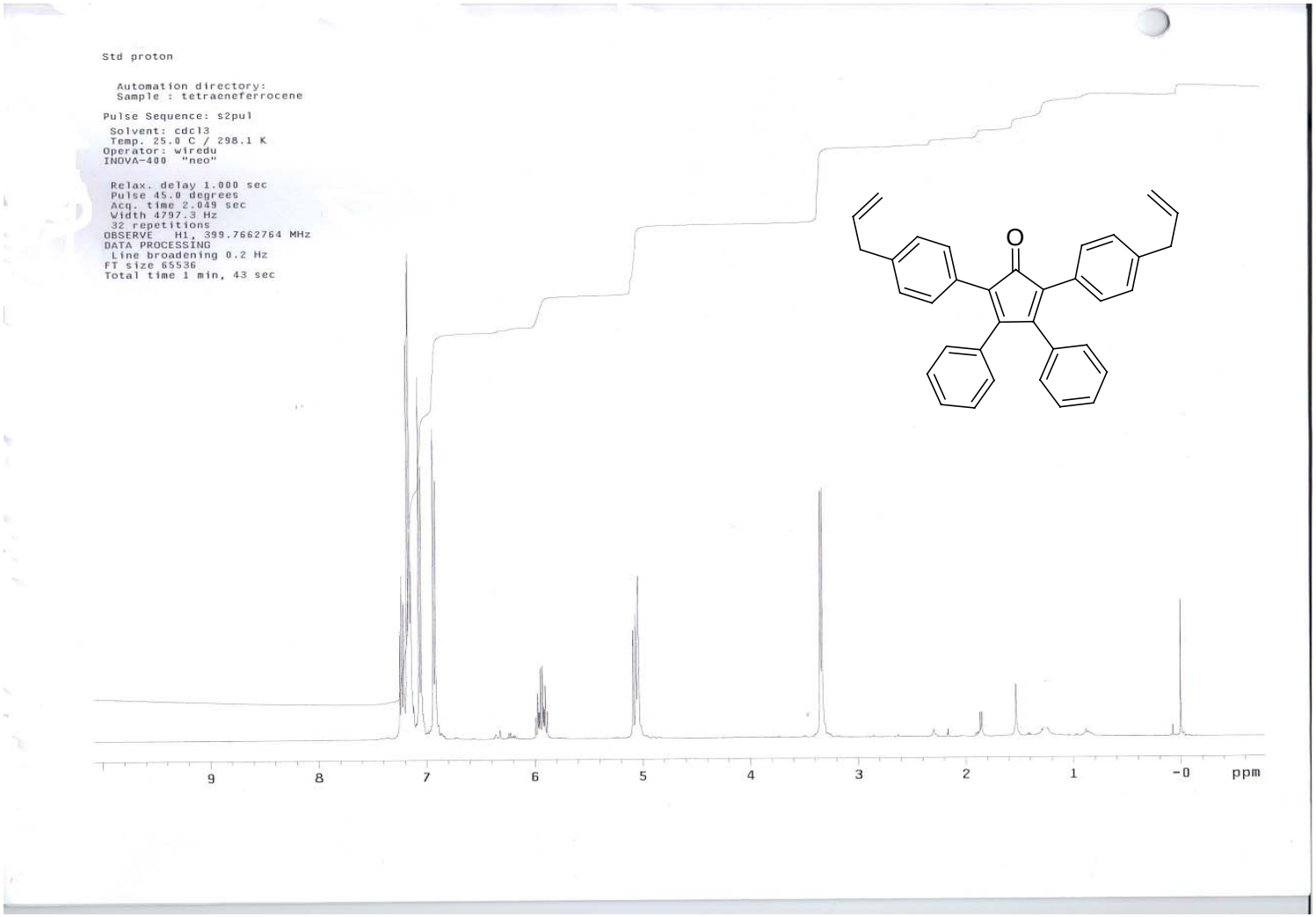
Acquisition Time (sec)	1.3582	***Comment***	Std proton			***Date***	Sep 18 2007	
Frequency (MHz)	100.53	***Nucleus***	13C	***Number of Transients***	5000	***Original Points Count***	31375	***Points Count*** 32768
Solvent	cdcl3	***Sweep Width (Hz)***	24125.45			***Temperature (grad C)***	25.000	



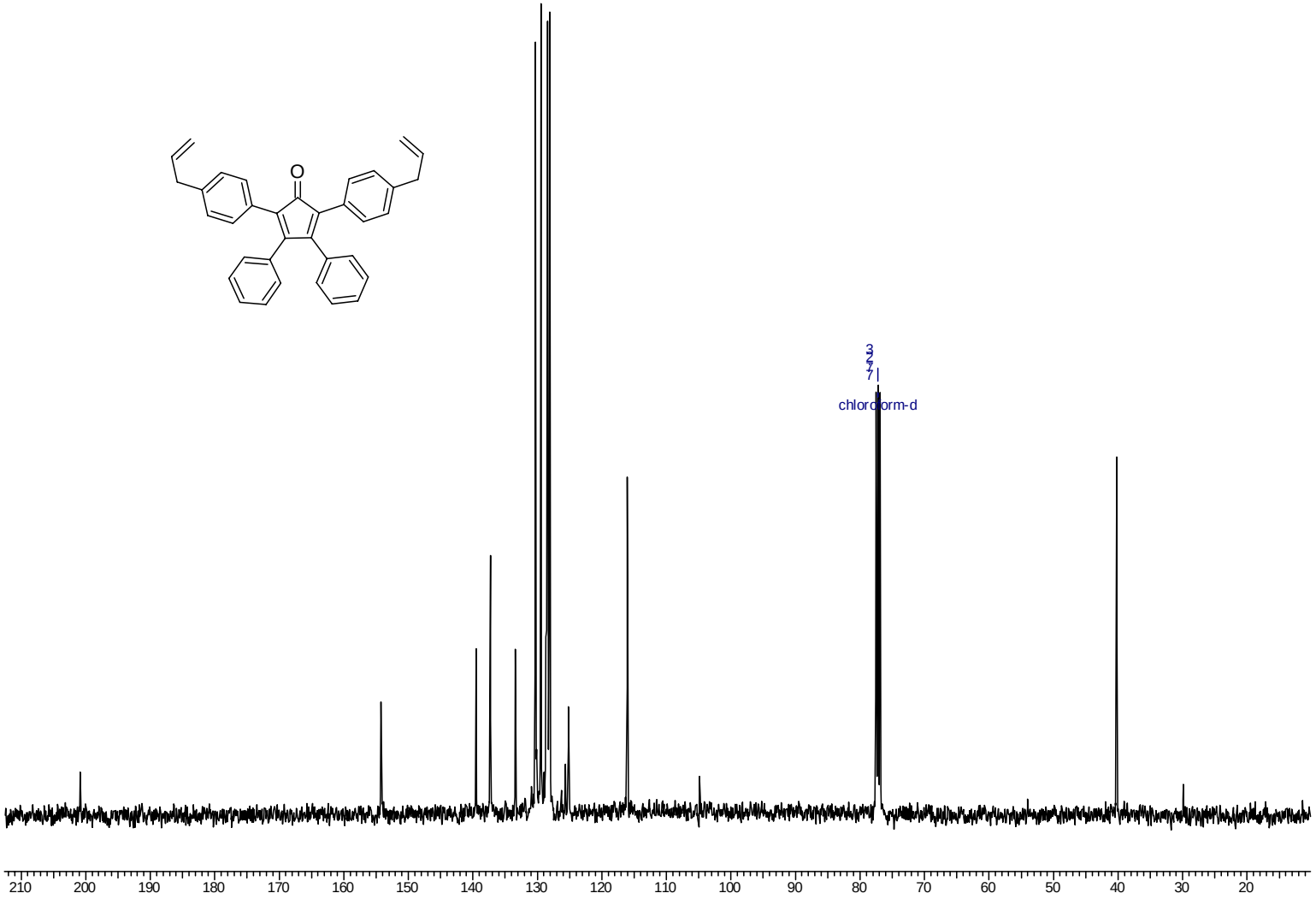
Acquisition Time (sec)	2.7304	***Comment***	STANDARD 1H OBSERVE			***Date***	Sep 20 2007
Frequency (MHz)	199.98	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	5984
Solvent	CDCl3	***Sweep Width (Hz)***	3000.30	***Temperature (grad C)***	29.000		



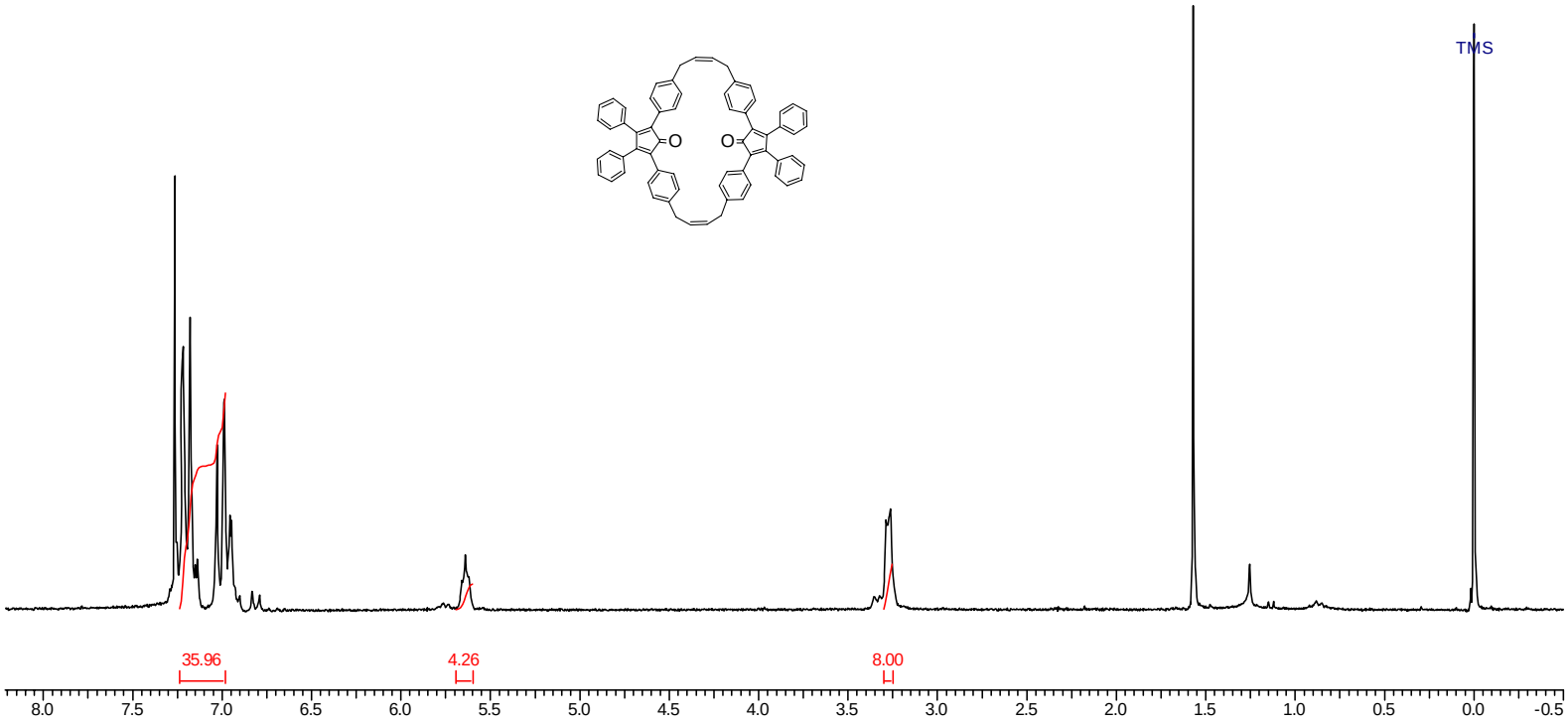
Appendix B - ^{1}H and ^{13}C NMR for Chapter 3



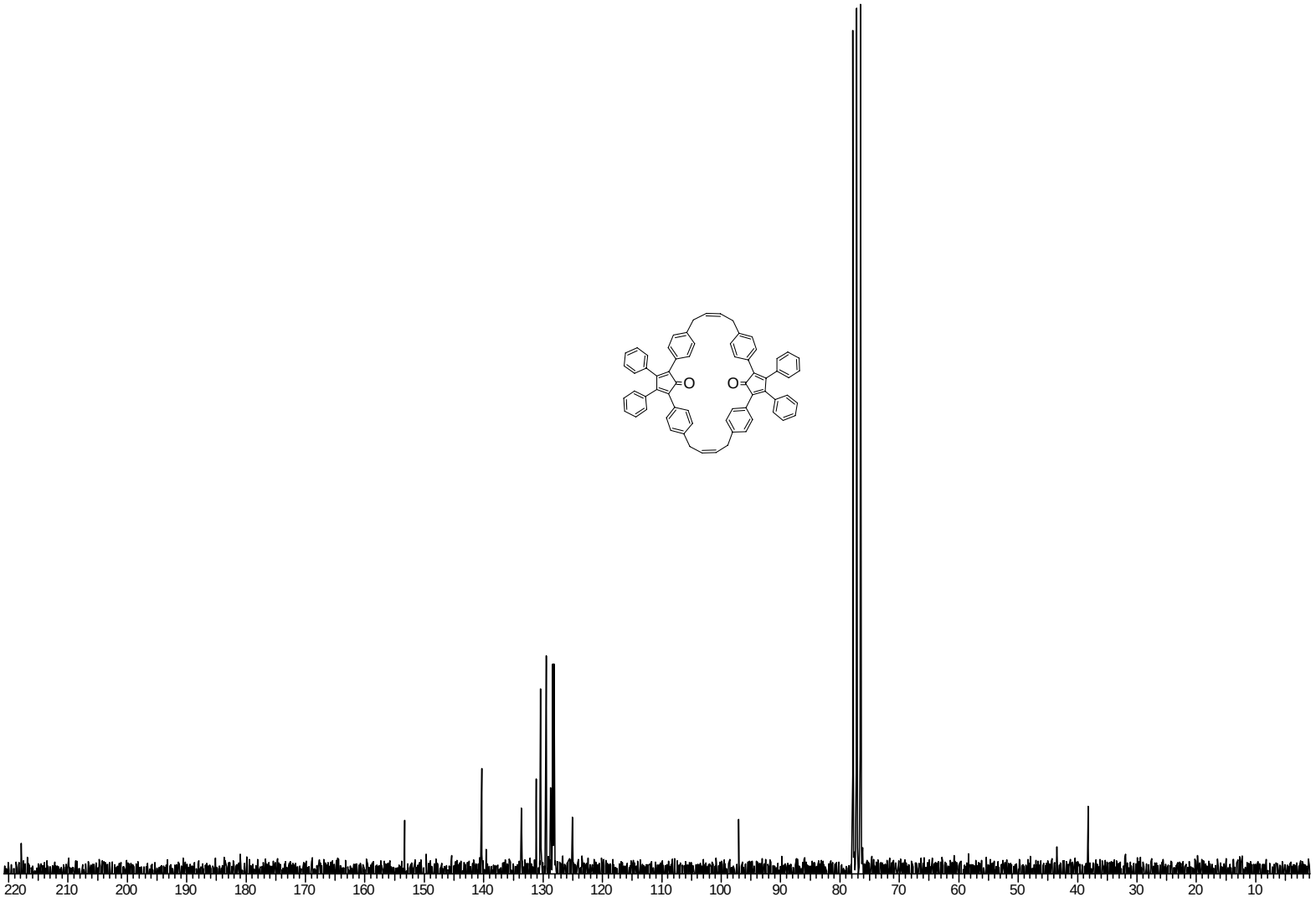
Acquisition Time (sec)	1.3582	***Comment***	Std proton		***Date***	Sep 8 2007	
Frequency (MHz)	100.53	***Nucleus***	13C	***Number of Transients*** 14888	***Original Points Count***	31375	***Points Count*** 32768
Solvent	CDCl3	***Sweep Width (Hz)***	24125.45		***Temperature (grad C)***	25.000	



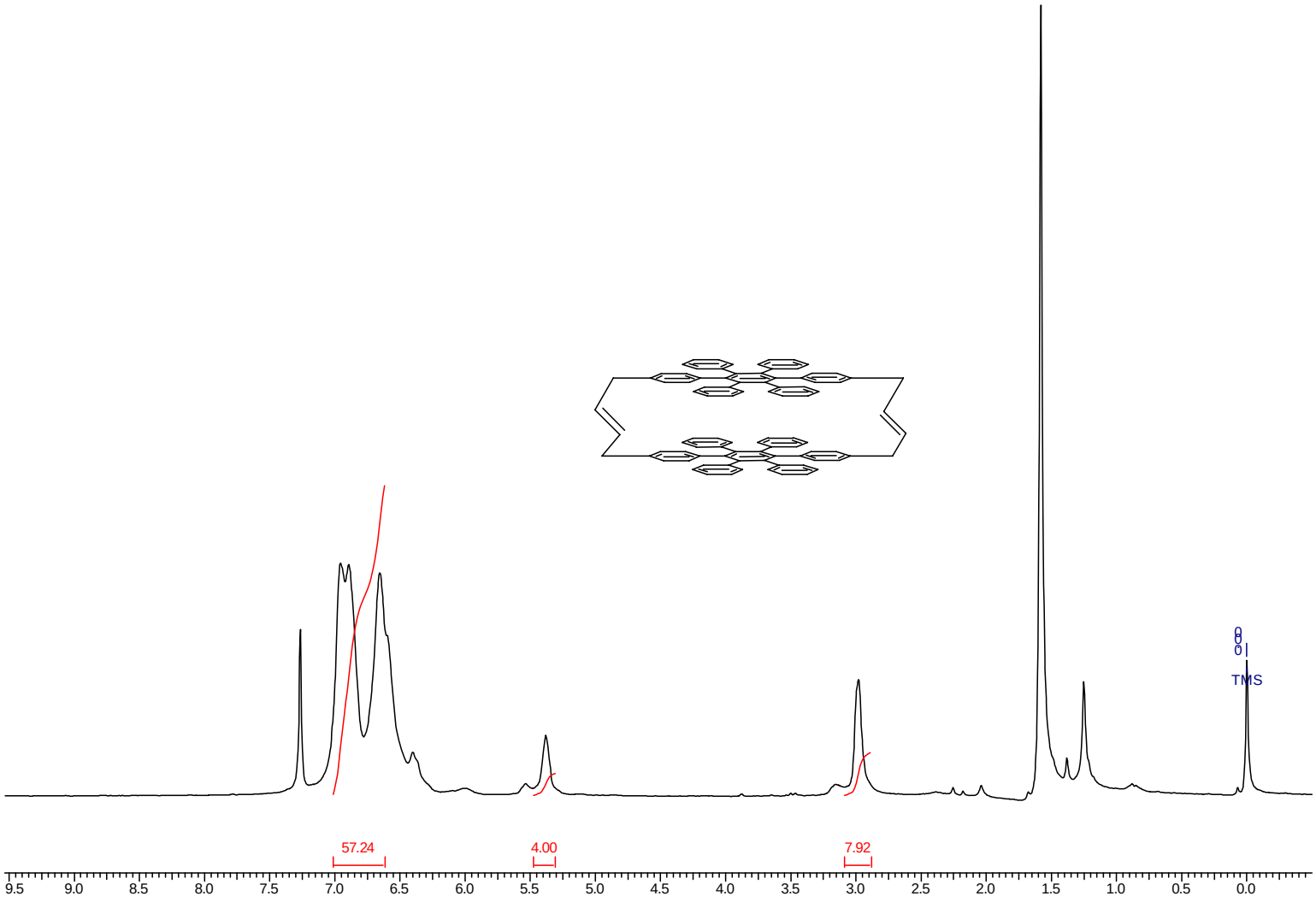
Acquisition Time (sec)	2.7304	***Comment***	STANDARD 1H OBSERVE			***Date***	Jul 31 2008	
Frequency (MHz)	199.98	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	5984	***Points Count***	8192
Solvent	CDCl3	***Sweep Width (Hz)***	3000.30	***Temperature (grad C)***	29.000				



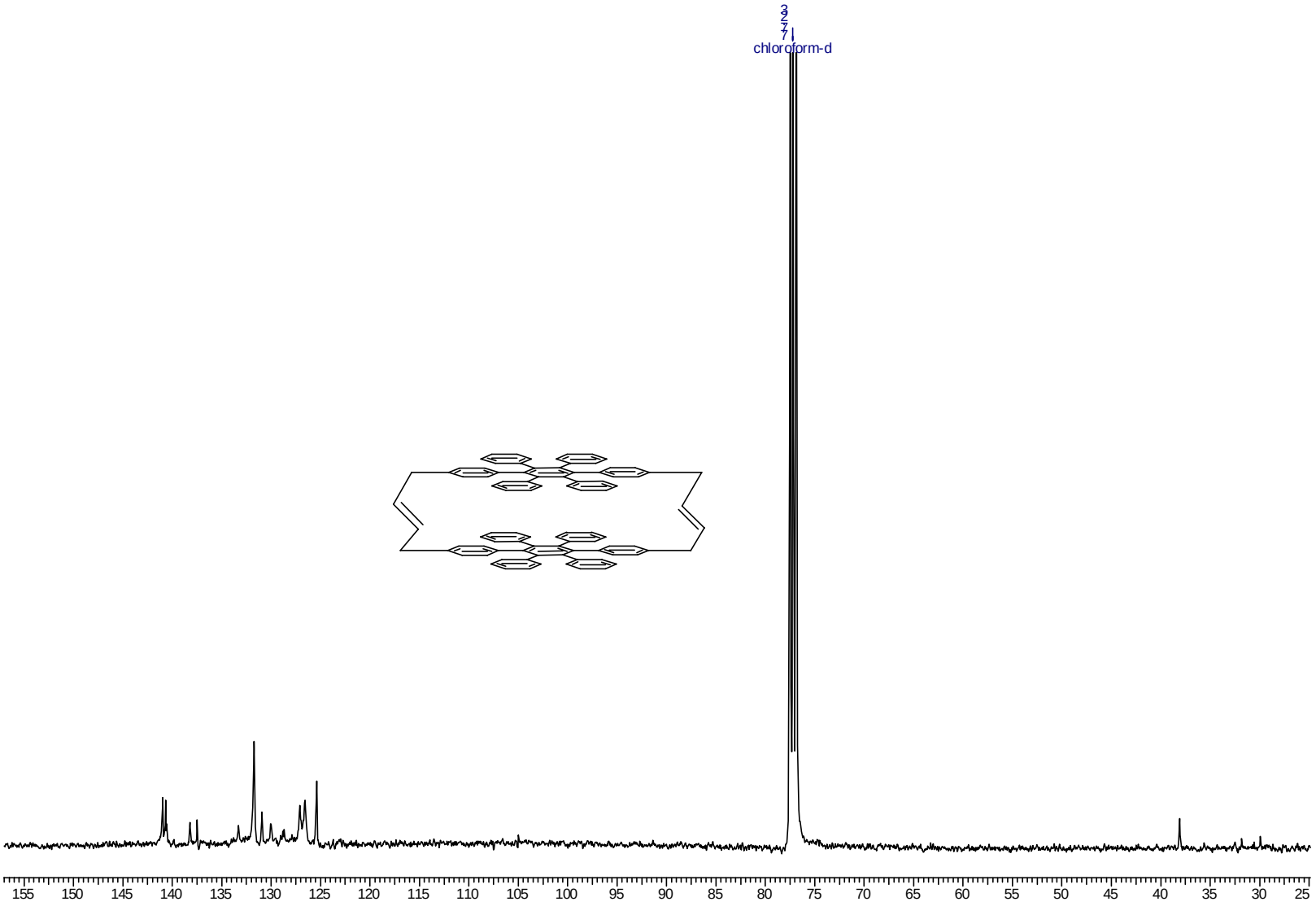
Acquisition Time (sec)	2.6214	***Comment***	13C OBSERVE			***Date***	Jul 30 2008		
Frequency (MHz)	50.29	***Nucleus***	13C	***Original Points Count***	18720	***Points Count***	32768	***Solvent***	CDCl3
Sweep Width (Hz)	12500.00			***Temperature (grad C)***	29.000				



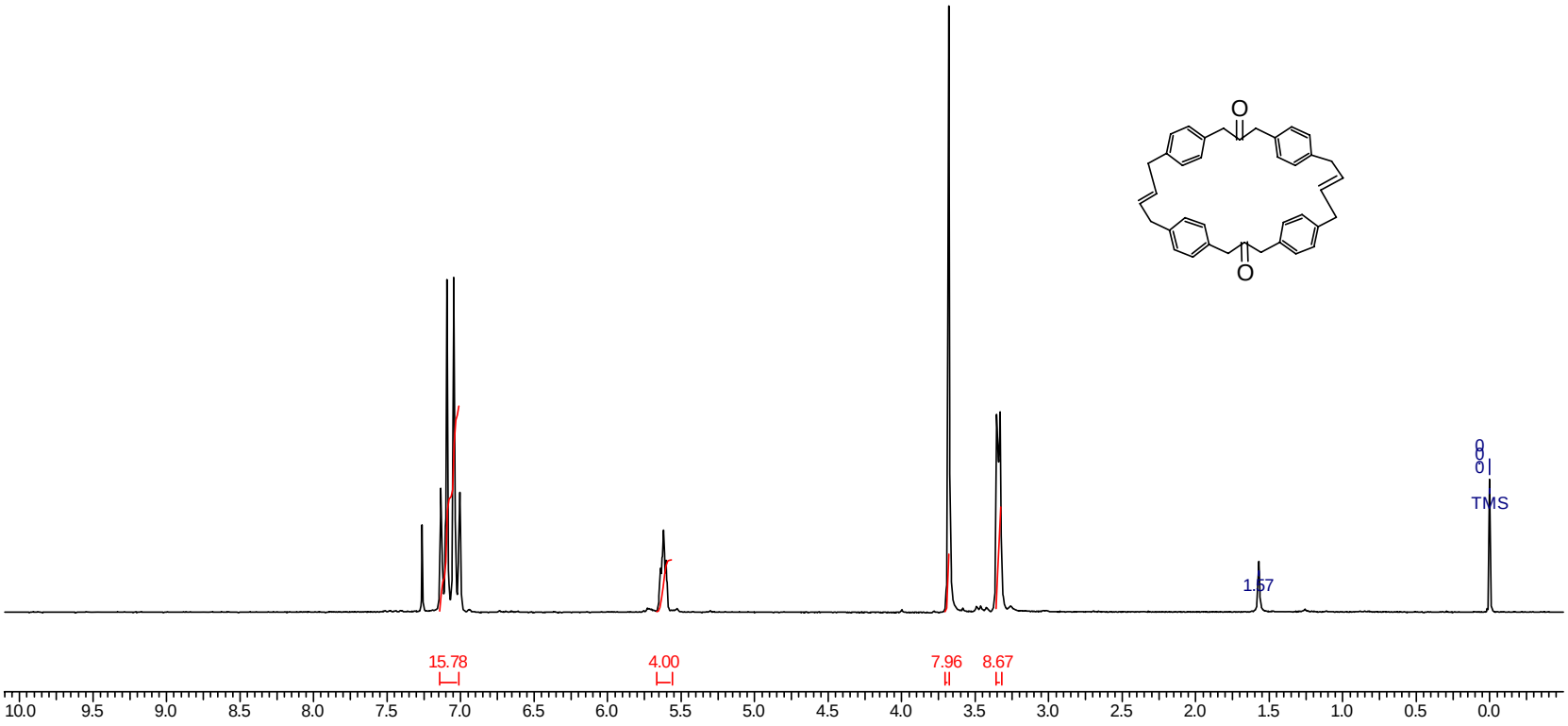
Acquisition Time (sec)	2.7304	***Comment***	STANDARD 1H OBSERVE			***Date***	Jul 3 2008
Frequency (MHz)	199.98	***Nucleus***	1H	***Number of Transients***	200	***Original Points Count***	5984
Solvent	CDCl3	***Sweep Width (Hz)***	3000.30	***Temperature (grad C)***	29.000		



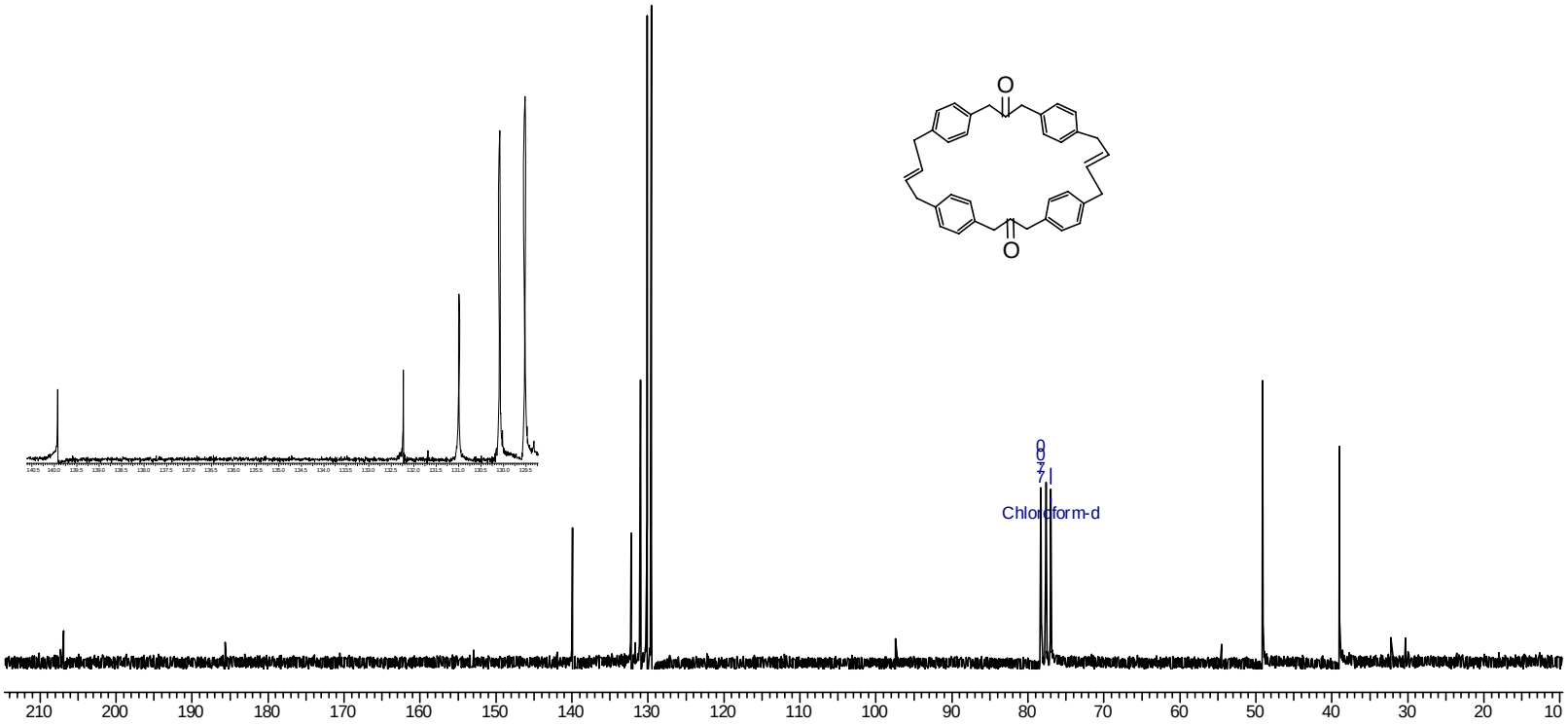
Acquisition Time (sec)	1.3582	***Comment***	Std proton			***Date***	Jul 4 2008
Frequency (MHz)	100.53	***Nucleus***	13C	***Original Points Count***	31375	***Points Count***	32768
Sweep Width (Hz)	24125.45			***Temperature (grad C)***	25.000		



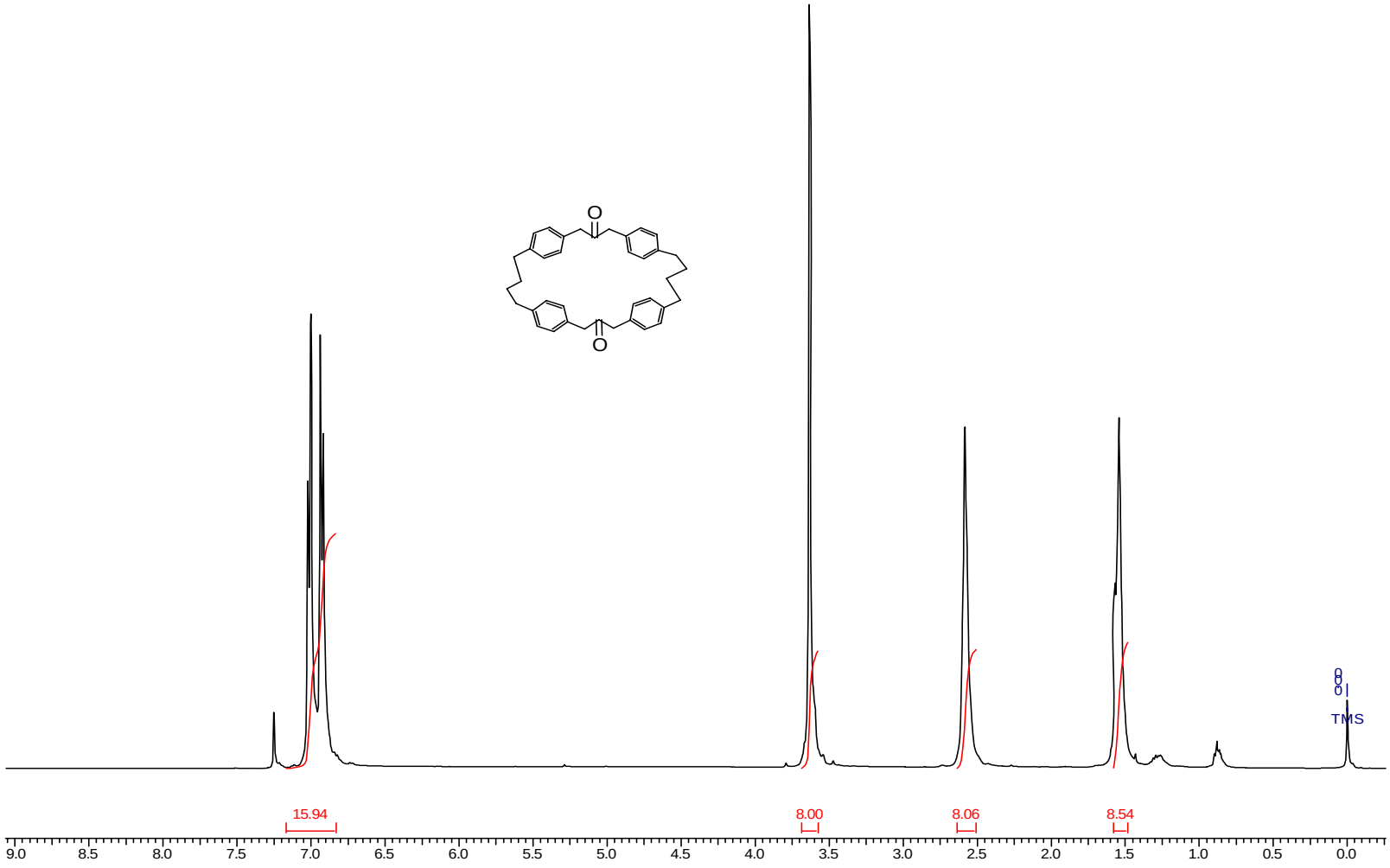
Acquisition Time (sec)	2.7304	***Comment***	STANDARD 1H OBSERVE			***Date***	Jul 28 2008
Frequency (MHz)	199.98	***Nucleus***	1H	***Number of Transients***	100	***Original Points Count***	5984
Solvent	CDCl3	***Sweep Width (Hz)***	3000.30	***Temperature (grad C)***	29.000		



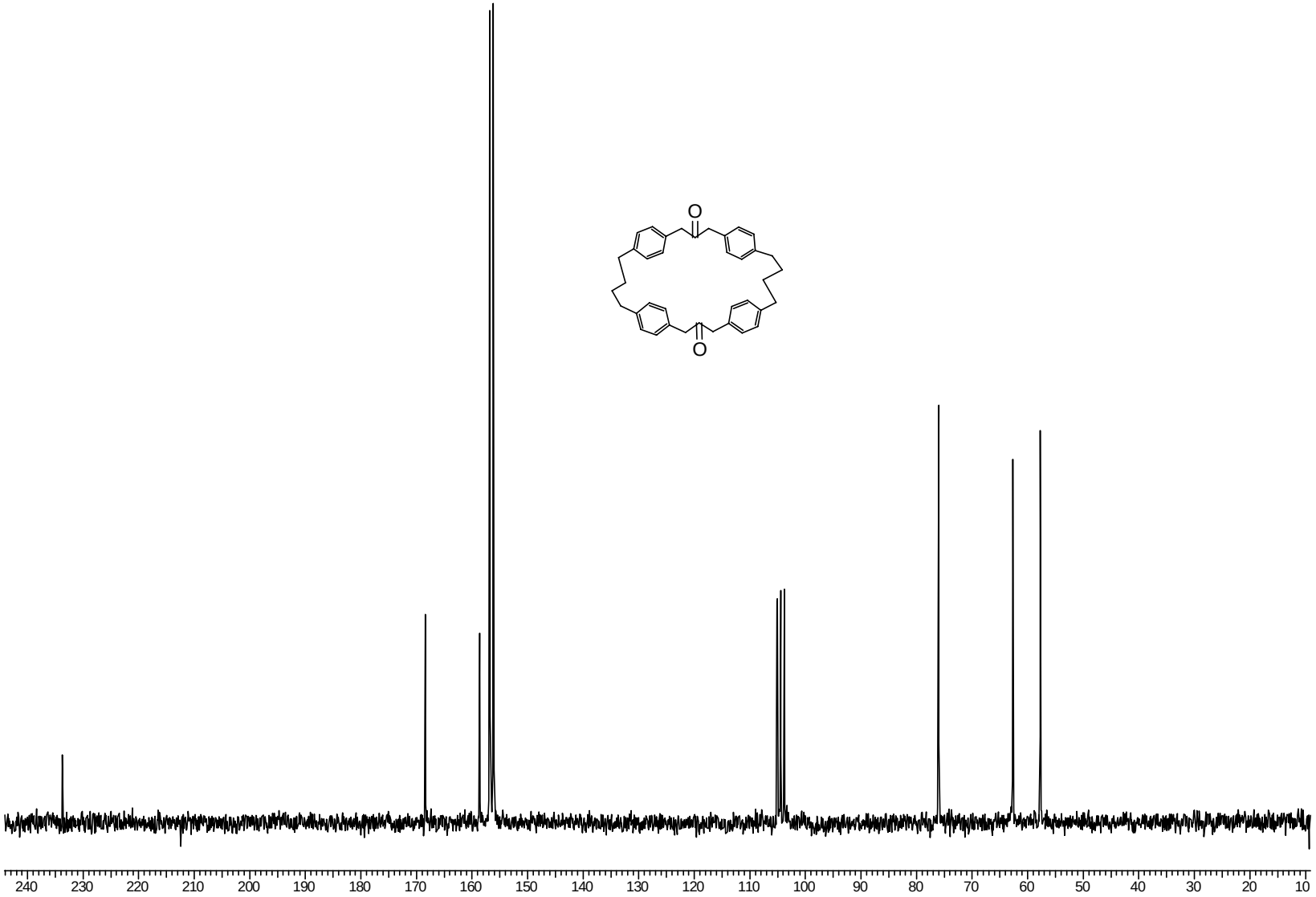
Acquisition Time (sec)	2.6214	***Comment***	13C OBSERVE			***Date***	Jul 10 2008		
Frequency (MHz)	50.29	***Nucleus***	13C	***Original Points Count***	18720	***Points Count***	32768	***Solvent***	CDCl3
Sweep Width (Hz)	12500.00			***Temperature (grad C)***	29.000				



Acquisition Time (sec)	2.0492	***Comment***	Std proton			***Date***	Sep 17 2008			***Frequency (MHz)***	399.76
Nucleus	1H	***Number of Transients***	100	***Original Points Count***	8189	***Points Count***	8192	***Solvent***	CDCl3	***Sweep Width (Hz)***	3997.60
Temperature (grad C)	25.000										



Acquisition Time (sec)	2.6214	***Comment***	13C OBSERVE		***Date***	Sep 17 2008	
Frequency (MHz)	50.29	***Nucleus***	13C	***Number of Transients*** 10000	***Original Points Count***	18720	***Points Count*** 32768
Solvent	CDCl3	***Sweep Width (Hz)***	12500.00		***Temperature (grad C)***	29.000	



Acquisition Time (sec)	2.5616	***Comment***	Std proton		***Date***	Nov 21 2008	
Frequency (MHz)	399.76	***Nucleus***	1H	***Number of Transients*** 120	***Original Points Count***	13103	***Points Count*** 16384
Solvent	CDCl3	***Sweep Width (Hz)***	6395.91		***Temperature (grad C)***	25.000